Atomic and electronic structures of the group-IV elements on Si(111)-(√3×√3) surface

S. Özkaya1,2, M. Çakmak1 and B. Alkan3
1 Department of Physics, Gazi University, 06500 Ankara, Turkey
2 Department of Physics, Aksaray University, 68100 Aksaray, Turkey
3 Department of Engineering Physics, Ankara University, 06100 Ankara, Turkey
E-mail: cakmak@gazi.edu.tr

Abstract. We have examined the Si(111) surface with 1/3 monolayer of group-IV elements within the ab initio density functional theory. We have considered two possible threefold-coordinated sites for the atom adsorption: (i) \( H_3 \) site (this site is directly above a fourth-layer Si atom and (ii) \( T_4 \) site (directly above a second-layer Si atom). For the atoms Ge, Sn, and Pb, the \( T_4 \) position always gives the most stable configuration, comparing with the \( H_3 \) site. The calculated energy difference between \( T_4 \) and \( H_3 \) for Pb, Ge, and Sn, is 0.32 eV, 0.59 eV, and 0.41 eV, respectively. We have also presented electronic band structure and orbital character of the surface states of the Sn/Si(111)-(√3×√3) surface.

1. Introduction
Group-IV elements on Si(111) surface have been intensively studied because of their importance in both scientific interest and potential applications in the integrated circuit industry. Deposition of group-IV atoms, such as Pb, Ge, and Sn result in different reconstructions of the Si(111) surface, depend on temperature and coverage. It is well known that at the room temperature 1/3 monolayer coverage of group-IV elements on Si(111) and Ge(111) surfaces induces a (\( √3 \times √3 \)) reconstruction [1, 2, 3], as group-III and V elements. In addition, this structure has also attracted great attention due to structural phase transition observed at low temperatures [4].

The ordered-reconstruction obtained by the reaction of Pb, Ge, and Sn with a Si(111) surface, the so-called X/Si(111)-(√3×√3) [X stands for Ge, Sn, and Pb], has been studied with a variety of surface-sensitive techniques: low-energy electron diffraction (LEED) [5, 6], angle-resolved photoemission spectroscopy (ARUPS) [7, 8], scanning tunneling microscopy (STM) [4, 5, 9], high-resolution core-level spectroscopy [2, 10], non-contact atomic force microscopy (NC-AFM) [11, 12], and X-ray standing waves (XSW) [1].

The general consensus is that the group-IV metals/Si(111)-(\( √3 \times √3 \)) structure has some high-symmetry locations, like \( T_4 \), \( H_3 \), and \( S_5 \), for the chemisorption of the adatom. In the \( T_4 \) and \( H_3 \) models, the adatom locates directly above a second-layer Si atom and a fourth-layer Si atom, respectively. In the \( S_5 \) model, the adatom is substituted to the second-layer Si site of the substrate while a silicon atom fills the \( T_4 \) site just above the adatom. Theoretical studies which use the \( ab \ initio \) pseudopotential method and experimental technique show that \( T_4 \) geometry has the most probable geometry of the group-IV elements on the Si(111) surface apart from the...
C atom. The C atom prefers the $S_3$ geometry as the most stable binding site, resulting from its smaller radius, in a similar manner for Boron atom [13, 14].

The electronic structure of the group-IV elements on the Si(111)$((\sqrt{3}\times\sqrt{3})$ surface has a similar behavior to the electronic structure for the group-III on the Si(111)$((\sqrt{3}\times\sqrt{3})$ surface. In order to explain the source of the surface states of these structures it is necessary to depict their charge density contour plots. To our knowledge, we note that there is not a comprehensive theoretical work in the field. The aim of this work is to make the detailed structural and electronic analysis of the X/Si(111)$((\sqrt{3}\times\sqrt{3})$ surfaces, and particularly to explain the orbital character of the surface states.

2. Method
In the present work, all the calculations have been carried out using the Vienna *ab initio* simulation package (VASP) [15, 16, 17, 18] based on the density functional theory (DFT). Within this method, the Kohn-Sham single particle functions were expanded in a basis of plane waves up to cut-off energy of 25 Ry. This cut-off was found to be adequate for the structural studies as well as for the electronic structure. We do not find any significant changes in the key parameters when the energy cut-off is increased from 25 Ry to 30 Ry. For electron exchange and correlation terms, Perdew and Zunger-type functional [19, 20] was used within the generalized gradient approximation (GGA) [21] including non-linear core correction. Self-consistent solutions were obtained by employing the $(4\times4\times1)$ Monkhorst-Pack [22] grid of k-points for the integration over the Brillouin Zone for the $(\sqrt{3}\times\sqrt{3})$ surface reconstructed unit cell.

The surface was modeled in repeated slab geometry. Each slab consists of seven (111) layers of Si atoms and neighboring slabs are separated by empty space 8 atomic layers wide. Two back substrate-layers were frozen into their bulk positions, and each Si atom at the back surface was saturated with one hydrogen atoms. All the remaining substrate atoms, the adsorbate atoms and the saturating H atoms were allowed to relax into their minimum energy positions. The theoretical bulk lattice constant 5.46 Å was used in the surface calculations. This value is in agreement with other theoretical result [23] using the pseudopotential method, and were used in performing the surface calculations. This value is also within 0.5% of experimental results.

3. Results and Discussions
Similar to the group IIIA metal atoms, we have considered two possible adsorption sites (i.e., $H_3$ and $T_3$) for X-induced Si(111)$((\sqrt{3}\times\sqrt{3})$ reconstruction using 1/3 monolayer of X. The optimized structural models for these binding sites has been given schematically in Fig.1 (a)-(b), respectively. We have carried out total-energy calculations for both geometries using the pseudopotential method and the GGA. In all of the X-induced $(\sqrt{3}\times\sqrt{3})$ reconstructions, upon relaxation it was found that the $T_4$ geometry has the lowest total energy compared to that of the $H_3$ model. For example, for the Pb/Si(111)$((\sqrt{3}\times\sqrt{3})$, -Ge, and -Sn surfaces, the resultant total energy for the $T_4$ model is 0.32 eV/adatom, 0.59 eV/adatom, and 0.41 eV/adatom lower, respectively. For the $T_4$ and $H_3$ models, we have labeled the bond length between the adatom and the three surface Si atoms to be $a$, $b$, and $c$, while we have denoted the vertical distance between the adatom and the second-layer Si atom at the $T_4$ position as $d_{13\perp}$ and we have also labeled the relative vertical distance due to the relative moving of the Si atoms in the second layer substrate as $d_{33\perp}$. The relaxed geometry parameters of the $T_4$ and $H_3$ models are shown in Fig.1 and their values are also given in Table I.

By examining closely the structural properties of the Pb/Si(111)$((\sqrt{3}\times\sqrt{3})$ surface for the $T_4$ model we have found that the bond length, represented $a$, $b$, and $c$, are 2.89 Å, 2.90 Å, and 2.90 Å, respectively, and that the vertical distance $d_{13\perp}$ is 2.64 Å. Besides, the second layer Si atoms of the substrate is not flat, but not for the $H_3$ model. Si atom which is just below the Pb adatom at the $T_4$ position moves downward by 0.41 Å relative to the other Si atom. These
Figure 1. Schematic side view and top view of the X/Si(111)-(√3×√3) surface, (a) H₃ and (b) T₄. The (111)-(√3×√3) has a rotation angle of 30 degrees with respect to 1×1.

Figure 2. Electronic band structure of the T₄ site for Sn/Si(111)-(√3×√3) surface. The thick represent surface bands. The thin lines region is the bulk (√3×√3)-projected band structures for Si. The experimental results of Kinoshita et al. [7] and theoretical results of Profeta et al. [26] are indicated triangular and circular symbols, respectively.

Table 1. The calculated atomic key parameters (in Å) and the relative energies for the models shown in Fig.1.

| X   | Models | a   | b   | c   | d₁₃,⊥ | d₃₃',⊥ | Δ E (eV) |
|-----|--------|-----|-----|-----|-------|--------|----------|
| Pb  | H₃     | 2.93| 2.92| 2.92| 2.71  | 0.00   | 0.32     |
|     | T₄     | 2.89| 2.90| 2.90| 2.64  | 0.41   | 0.00     |
| Ge  | H₃     | 2.66| 2.66| 2.66| 2.44  | 0.00   | 0.59     |
|     | T₄     | 2.62| 2.62| 2.62| 2.55  | 0.58   | 0.00     |
| Sn  | H₃     | 2.84| 2.84| 2.84| 2.64  | 0.00   | 0.41     |
|     | T₄     | 2.80| 2.81| 2.80| 2.51  | 0.38   | 0.00     |

results are in agreement with the recent theoretical work of Chan et al [24]. They found that the T₄ structure was the most energetically favorable than the H₃ model. They also determined the key structure parameters a, b, and c, as 2.80 Å while the vertical distance d₁₃,⊥ was 2.93 Å. In addition, it was also reported that the relative distance between Si atoms in the second layer was 0.46 Å.

As it is seen from Table I, the Ge atom at the T₄ position is bonded to three surface Si atoms, labeled a, b, and c, at equal distance of 2.62 Å. The other structural parameters, such as d₁₃,⊥ and d₃₃',⊥, are 2.55 Å and 0.58 Å, respectively. Our results are in good agreement with
the experimental and theoretical work recently made by Quin et al [25]. In that work, it was reported that the \( T_4 \) model was energetically more favorable than the \( H_3 \) model, by about 0.60 eV/atom and the bondlengths, \( a \), \( b \), and \( c \), were the same as 2.61 Å. In addition, it was also determined that the second layer Si atom at the \( T_4 \) site moved downward relative to the other Si atoms, by about 0.40 Å.

On the other hand, for Sn/Si(111)-\((\sqrt{3} \times \sqrt{3})\) surface we calculated the structure parameters, \( a \), \( b \), \( c \), \( d_{13,\perp} \), and \( d_{33',\perp} \) to be 2.80 Å, 2.81 Å, and 2.80 Å, 2.51 Å, and 0.38 Å, respectively. These parameters are in agreement with the result obtained by Escuadro et al [1]. They found that the Sn–Si bond lengths, \( a \), \( b \), and \( c \), were in the interval 2.84 Å–2.68 Å, while the \( d_{33',\perp} \) was 0.26 Å.

In order to discuss the electronic properties of the group-IV on the Si(111) surface we have focused on the most favorable reconstruction model \( T_4 \). Because of the fact that all the group-IV elements had a similar characteristic behavior in terms of the electronic band structure, we have only examined the dispersion of the surface states of the Sn/Si(111)-\((\sqrt{3} \times \sqrt{3})\) structure shown in Fig.2. We have determined one unoccupied surface states, represented \( S_1 \), located below the bulk conduction band minimum, and two occupied surface state, represented \( S_2 \) and \( S_3 \), below the bulk valence band state maximum. As seen in Fig.2, our results are in good agreement with the experimental and previous theoretical works [7, 26]. Our calculation also show that the Sn–Si bond lengths, \( a \), \( b \), and \( c \), were in the interval 2.84 Å–2.68 Å, while the \( d_{33',\perp} \) was 0.26 Å.

To determine the nature of the surface states, we have plotted the total and partial charge density at the \( \bar{K}' \) point within the surface unit cell, and shown these plots in Figs.3(a) to (d). Fig.3(b) shows that the unoccupied surface state \( S_1 \) originates from the \( p_z \) orbital of Sn atom. This state is also a partially filled one, because the Sn atom has one more valence electron than the group-III element. This property results in the metallic behavior of the Sn/Si(111)-\((\sqrt{3} \times \sqrt{3})\) surface. The state \( S_1 \) actually disperses nearly 0.5 eV. The same value has been also reported by Profeta et al [26]. They also calculated the charge density for the \( S_1 \) state.

In addition, we have focused on the two occupied surface states \( S_2 \) and \( S_3 \) and shown the corresponding partial charge density contour plots in Figs.3(c) to (d). As seen from these Figures, the surface states, \( S_2 \) and \( S_3 \) arise from \( \sigma \)-type bonds between the \( p \)-orbital of the adatom and surface dangling bonds. While the highest occupied surface state \( S_2 \) has some contribution from
the $p$-orbital of the second layer Si atoms, the lower occupied state $S_3$ has no similar contribution from that of the second layer Si atoms. Besides, the occupied state $S_2$ disperses downward from $\bar{M}'$ point to $\bar{K}'$ point, with a bandwidth of 0.20 eV, while the other occupied state $S_3$ has a dispersion less than the $S_2$ dispersion.

4. Summary
From first-principles theoretical study we have presented the details of the atomic geometry and electronic states for the group-IV/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface. We considered the two possible adsorption site: $H_3$ and $T_4$. We have found that the energy difference between $T_4$ and $H_3$ for Pb, Ge, and Sn, is 0.32 eV, 0.59 eV, and 0.41 eV, respectively. The surface band structures studies here are generally similar to each other. We have depicted the surface band structure and the orbital nature of the individual surface states.

5. Acknowledgment
This work was supported by Turkish State Planning Organization (Project Number: 2001K120590). M. Ç gratefully acknowledges Gazi University for the financial support under BAP project 05/2006-19 and 05/2007-41.

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