Growth of thallium overlayers on Si(100) surface: Ab initio molecular dynamics study∗

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Formation of thallium overlayers on the Si(100)2×1 surface has been studied using first-principles total-energy calculations. According to total-energy calculations and STM image modeling, thallium atoms should occupy the following positions on Si(100) surface: (i) valley-bridge (0.25 ML of thallium coverage); (ii) parallel Tl-Tl dimer in valley-bridge (0.5 ML); (iii) pedestal, valley-bridge and valley-bridge (0.75 ML); and (iv) pedestal and valley-bridge (1.0 ML). The simulated STM images are in good agreement with experimental data [A.A. Saranin et al. Phys. Rev. B 71, 035312 (2005)]. The possible atomic mechanism of reconstruction alternation is discussed.

Keywords: Density functional calculations; Growth; Thallium; Si(100)

I. INTRODUCTION

Thallium is a group III metal with a peculiar chemistry, in that it can support a monovalent chemical state in addition to the more common trivalent state, as encountered with all the other group III elements [1]. Experimental investigations of thallium adsorption on Si(111) surface have been started in late 90’s [2–6] and revealed a number of interesting features in this surface system.

First paper on ab initio calculations of Tl/Si(111) adsorption system has been published by Ricart et al. [7]. Using Hartree-Fock method and very small clusters (up to 6 silicon atoms) they found that the T1 adsorption site is the most stable one on Si(111)-1×1. Further first principles simulations on Si(111)-1×1-Tl system conducted by Lee et al. [4] showed that T4 adsorption site is most energetically favorable for thallium.

In recent study [8] of thallium overlayers on Si(100) surface a number of surface reconstructions have been observed using scanning tunneling microscopy (STM). According to experimental data α-2×2-Tl, β-2×2-Tl, γ-2×2-Tl and 2×1-Tl surface structures corresponded to the thallium coverage of 0.25, 0.5, 0.75 and 1.0 ML, respectively. Present work is devoted to determination of atomic structures of above reconstructions using total-energy calculations based on the local density approximation.

II. METHOD OF CALCULATIONS

To find the energetically favorable structures we have performed ab initio total-energy calculations using the FHI96MD code [9] in which the CarParrinello type of electronic structure calculation [10] was used. The local density approximation (LDA) after CeperleyAlder [11] in the PerdewZunger parametrization [12] for the exchange and correlation functional and fully separable Troullier-Martins [13] pseudopotentials were employed.

The pseudopotentials were constructed using the FHI98PP code [14] and verified to avoid ghost states and to describe the basic experimental characteristic of bulk materials. The 5d states of thallium were treated as valence states.

The surface was simulated by a periodic slab geometry with a 2×1 (or 2×2) unit cell containing five silicon atomic layers and top Tl layer. The dangling bonds of the bottom slab layer were saturated by hydrogen atoms. The hydrogen atoms and bottom layer silicon atoms were fixed and the rest atoms were free to move. A vacuum region of approximately 9 Å was incorporated within each periodic unit cell to prevent interaction between adjacent surfaces. The cut-off energy of 35 Ry was applied in all calculations presented. Model STM images have been plotted as the density of states of the surface, summed up over the energy interval [15, 16].

The test calculations for Si(111)-1×1-Tl surface at 1 ML of thallium coverage have been carried out. Recent ab initio simulations for this system [4] showed that the

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FIG. 1: High-symmetry adsorption sites on Si(100)-2×1 surface: P - pedestal, B - bridge, C - cave, VB - valley-bridge.
T4 site is more stable for thallium atom than H3 site by 0.1 eV. We obtained the energy difference of 0.11 eV that is close to the value of Lee et al. [4].

III. RESULTS AND DISCUSSION

According to Ref. [8], surface unit cells for α-2 × 2-Tl, β-2 × 2-Tl, γ-2 × 2-Tl and 2 × 1-Tl reconstructions contain 1, 2, 3, and 2 thallium atoms, respectively. To find out atomic structures for above Tl/Si(100) reconstructions we conducted total-energy calculations for different structures with Tl atoms or dimers placed in high-symmetry adsorption sites on Si(100)-2 × 1 shown in Fig. 1: pedestal (P), valley-bridge (VB), bridge (B) and cave (C). The orientation of thallium dimers could be chosen both parallel (so-called para-dimers) and perpendicular (ortho-dimers) to the silicon substrate dimers. Total number of verified structures for four reconstructions is more than 40. Figures 2, 4, 5, and 7 show atomic configurations with energies close to the minimum energy for systems considered.

Figure 2 shows possible structures for α-2 × 2-Tl reconstruction with energies relative to the minimum energy structure. One can see that two structures with thallium atoms in valley-bridge and in cave have close energies. As the accuracy of our LDA total energy calculations is worse than 0.05 eV, we should undertake additional investigations to decide whether thallium atom occupies valley-bridge or cave adsorption site.

The most convenient method to make such decision is STM image modeling for both possible structures. Figure 3 shows the location of STM empty state protrusions [8] and the simulated model images for tip bias of −1.9 V. Obviously, the STM model image of structure with Tl atom in VB site represents the same locations of protrusions as the experimental picture. Thus, in α-2 × 2-Tl reconstruction thallium atoms occupy VB positions. The analysis of filled state images confirms this conclusion.

The next reconstruction β-2 × 2-Tl has been observed...
FIG. 4: $\beta-2 \times 2$-Tl reconstruction: relative energies for atomic configurations with following positions of thallium atoms: (a) valley-bridge para-dimer, (b) rotated dimer in cave, (c) bridge ortho-dimer, and (d) pedestal and valley-bridge. For structures (a), (b) and (c) the lengths of thallium dimers $d_{\text{Tl-Tl}}$ are presented.

FIG. 5: $\gamma-2 \times 2$-Tl reconstruction: relative energies for atomic configurations with following positions of thallium atoms: (a) pedestal, pedestal, and valley-bridge, (b) pedestal, valley-bridge, and valley-bridge, (c) pedestal and valley-bridge para-dimer, (d) valley-bridge and valley-bridge para-dimer, (e) pedestal and valley-bridge ortho-dimer, and (f) valley-bridge and pedestal ortho-dimer. For structures (c), (d), (e) and (f) the lengths of thallium dimers $d_{\text{Tl-Tl}}$ are presented.

At thallium coverage of 0.5 ML, energetically favorable structures containing two Tl atoms per surface unit cell are presented in Fig 4. In this case the decision on the most stable structure can be made using total-energy calculation data. Two thallium atoms form VB para-dimer with the length of 2.98 Å (see Fig. 4(a)). This is a typical structure for 0.5 ML $2 \times 2$ reconstruction of group III elements [17, 18] on Si(100) surface. The structure in Fig. 4(b) contains the thallium dimer rotated on the angle of 73°. It is resulted from non-equilibrium structures with thallium ortho- and para-dimers in cave.

To verify our conclusion on $\beta-2 \times 2$-Tl reconstruction we have plotted model STM images for minimum energy structure. According to the experimental data [8] empty-state protrusions occupy the pedestal sites and filled-state protrusions are in the valley-bridge sites. The model STM images show the same locations of protrusions. Therefore the total-energy calculations and STM image modelling allow us to conclude that thallium atoms should form VB para-dimer in valley-bridge positions at the coverage of 0.5 ML.

Figure 5 shows possible structures for $\gamma-2 \times 2$-Tl reconstruction obtained experimentally at 0.75 ML of thallium coverage. Energies of structures (a) and (b) are close to another, so in this case we made the comparison of model STM images with experimental ones for both
FIG. 6: The location of STM (a) filled and (d) empty state protrusions (in red) [8]. The model STM images for $\gamma$-$2 \times 2$-Tl structures with thallium atoms (marked by crosses) located in (b), (e) pedestal, pedestal, and valley-bridge and (c), (f) pedestal, valley-bridge, and valley-bridge.

filled and empty states. The simulated STM images and the location of experimentally observed protrusions are presented in Fig. 6. Only Tl atoms located in pedestal sites appear on both filled state (Figs. 6(b) and 6(c)) and empty state (Figs. 6(e) and 6(f)) model STM images. So, the pictures for P+P+VB case (Figs. 6(b) and 6(e)) look like $2 \times 1$ reconstruction, especially for empty states. Whereas model STM images for P+VB+VB case (Figs. 6(c) and 6(f)) reveal $2 \times 2$ visible pictures. Thus we can conclude that in atomic structure corresponded for $\gamma$-$2 \times 2$-Tl reconstruction thallium atoms occupy pedestal, valley-bridge, and valley-bridge positions.

The final reconstruction $2 \times 1$-Tl has arrangement of thallium atoms shown in Fig 7. They are located in pedestal and valley-bridge sites. The model STM images for $2 \times 1$-Tl reconstruction show the same location of protrusions as the experimental ones, namely pedestal sites for both empty-state and filled-state images [8]. Such structure is typical for $2 \times 1$ reconstruction of group I elements on Si(100) [19–22]. In this case thallium has a monovalent atom behavior.

It should be noted that in all observed cases the influence of thallium in both atomic and dimer forms on silicon substrate dimers is negligible. The variations of silicon dimer lengths never exceed 0.1 Å. So the change in thallium reconstructions never leads to modifying of substrate atomic structure.

Summarizing the study of atomic structure formation at different coverages we can suggest possible atomic mechanism of reconstructions changing. The atomic scheme for this process is shown in Fig. 8. First, Tl atoms occupy VB sites at 0.25 ML and form $\alpha$-$2 \times 2$-Tl reconstruction. Then at 0.5 ML thallium para-dimers arise and $\beta$-$2 \times 2$-Tl reconstruction appears. The most probable way for this is the migration of additional Tl atoms within troughs between silicon substrate dimer rows. According to experimental observations for $\alpha$-$2 \times 2$-Tl reconstruction [8] migrations of thalliums under STM tip has been observed along Si dimer rows only.

The next stage at 0.75 ML involves thallium para-dimers destruction and $\gamma$-$2 \times 2$-Tl reconstruction forming. Figure 8 shows two possible ways to do this via either of metastable 0.75 ML structures, containing VB para-dimer still. Both of these metastable structures (see Figs. 5(c) and 5(d)) have energy of approximately 0.1 eV greater than the minimum energy structure (Figs. 5(a)). The definition of intermediate atomic configuration requires additional study and the conclusion will depend on the energy barrier heights of Tl dimer destruction in both cases.

The final stage of 1 ML coverage forming includes the filling of vacant pedestal sites by Tl atoms, after that the $2 \times 1$-Tl reconstruction appears.

IV. CONCLUSIONS

In conclusion, according to our total energy calculations and STM image modeling, thallium atoms should occupy the following positions on Si(100) surface: (i) valley-bridge ($\alpha$-$2 \times 2$-Tl); (ii) parallel Tl-Tl dimer in valley-bridge ($\beta$-$2 \times 2$-Tl); (iii) pedestal, valley-bridge and valley-bridge ($\gamma$-$2 \times 2$-Tl); and (iv) pedestal and valley-bridge ($2 \times 1$-Tl).
FIG. 7: 2 × 1-Tl reconstruction: relative energies for atomic configurations with following positions of thallium atoms: (a) pedestal and valley-bridge, (b) pedestal and cave, (c) bridge and valley-bridge, and (d) bridge and cave.

FIG. 8: The sequence of Tl/Si(100) surface reconstructions at 0.25-1.0 ML thallium coverage. Possible intermediate metastable γ-2 × 2-Tl reconstructions correspond to Figs. 5(c) and 5(d).

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