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Structural and electronic properties of thallium overlayers on the Si(111)-7×7 surface

S. S. Lee, H. J. Song, N. D. Kim, and J. W. Chung*
Physics Department and Basic Science Research Institute, Pohang University of Science and Technology, San 31 Hyoja Dong, Pohang 790-784, Korea

K. Kong and D. Ahn
IQUIPS, University of Seoul, Seoul 130-743, Korea

H. Yi
Supercomputing Center, KISTI, P.O.Box 122, Yusung, Taejon 305-600, Korea

B. D. Yu
Department of Physics, University of Seoul, Seoul 130-743, Korea

Hiroshi Tochihara
Department of Molecular and Material Sciences, Kyushu University, Kasuga, Fukuoka 816-8580 Japan

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We have investigated atomic arrangements and their electronic properties of the well-ordered thallium overlayer structures formed on the Si(111)-7×7 surface. As for other trivalent atoms, Tl is found to form a well-defined $\sqrt{3}\times\sqrt{3}$ surface, indicating the absence of a so-called ''inert pair effect'' considered only for Tl. Another well ordered 1×1 surface at 1.0 monolayer appears to be semiconducting in our angle-resolved photoemission spectra dominated by a unique dispersive surface band near the Fermi level. Our theoretical calculations using density-functional theory show that Tl adatoms occupy the T_4 sites and saturate all the dangling bonds of surface Si atoms to make the surface semiconducting with a band gap of 0.34 eV. The filled surface band observed has been well reproduced in our band calculations.

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The interaction of group III elements with Si surfaces has been extensively studied mainly because of their technological relevance as dopant materials and the presence of various adsorbate-induced phenomena at semiconductor surfaces.[1] The adsorption of thallium (Tl) on the Si(111)-7×7 surface, in particular, is interesting since Tl has been known to behave quite differently from other group III elements in forming stable ordered surface structures;[2] the only ordered structure formed by Tl has been reported to be a 1×1 surface [hereafter denoted as a Tl/Si(111)-1×1 surface] at 1.0 monolayer(ML) in sharp contrast with a variety of different structures found for other group III elements such as Al and In.[1] The absence of other ordered structures by Tl has been considered to exhibit a so-called ''inert pair effect'' of a Tl atom where the $6s^2$ electrons are assumed to be inactive in chemical bonding with Si atoms. Tl, therefore, has been thought to act as a monovalent rather than trivalent atom on the Si(111) surface in a sense chemically close to the alkali metals or novel metals.[2] Because of the large atomic radius and the effectively monovalent character of Tl, the on-top site T_1 directly above the Si first layer of the unreconstructed 1×1 surface has been preferred as the binding site for Tl on the Si(111) surface.[3,4] In addition to the presence of interesting structures such as the superlattice of metallic nanodots at low coverage ∼0.2 ML[5] and the rotational epitaxy of an incommensurate Tl metallic overlayer,[4] the extremely inert nature of the Tl/Si(111)-1×1 surface is another reason why it is so interesting since it may serve as a stable substrate surface to form other atomic structures.

In this Brief Report we report results of combined studies for the atomic structures and their electronic properties of the ordered Tl overlayer structures focussed especially on the Tl/Si(111)-1×1 surface. We have determined surface bands of the 1×1 irreducible surface Brillouin zone (SBZ) from our angle-resolved photoemission spectroscopy (ARPES) measurements. The surface bands and the atomic structure of the Tl/Si(111)-1×1 surface have been well reproduced in our theoretical calculations using the density functional theory (DFT). We further show that there exists a stable well-defined $\sqrt{3}\times\sqrt{3}$ structure as observed for other group III elements. Our calculations also show that the T_4 site is the most stable for Tl on the Tl/Si(111)-1×1 surface in sharp contrast to previous studies.[2–4]

We have utilized a combination of several surface probing tools including low energy electron diffraction (LEED), x-ray photoemission spectroscopy (XPS), and ARPES to investigate structural and electronic properties of the ordered Tl overlayer structures on the Si(111)-7×7 surface.

The Si(111) sample was prepared by cutting a phosphorus-doped Si wafer with resistivity of ∼2 Ω cm into a ribbon shape of an area of 18×5 mm^2. The sample was cleaned by resistively heating up to 1100 °C for about 10 seconds followed by annealing at 700 °C for about 5 minutes. The Si(111) surface thus prepared produces a well-defined 7×7 LEED pattern with no detectable signals of the core level peaks of carbon or oxygen atoms in our XPS spectra. Deposition of Tl was made by flowing current through the tungsten filament ($\phi\sim0.025$ mm) wrapped around a Tl rod ($\phi\sim1.6$ mm). The sample was kept at 300 °C with pressure below 3×10^{-10} Torr during the deposition of Tl. The Tl

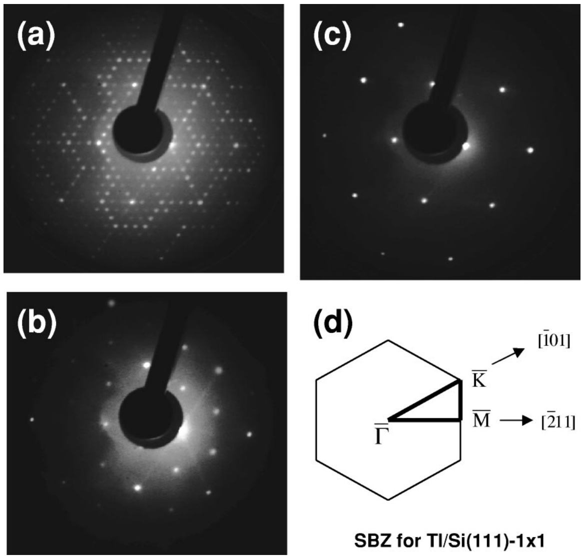

FIG. 1. Progressive development of LEED patterns with the adsorption of Tl. The clean Si(111)-7×7 (a) becomes a $\sqrt{3}\times\sqrt{3}$ structure (b) at 1/3 ML, which further develops into a 1×1 structure (c) at 1.0 ML. The LEED beam energy was 101 eV. The surface Brillouin zone (SBZ) for the Tl/Si(111)-1×1 structure (d) is drawn with thin lines while the irreducible part of the SBZ is depicted by thick lines.

coverage was estimated by measuring a work function change as a function of Tl exposure (not shown here). By normalizing the saturation coverage of Tl as 1.0 monolayer (ML), we estimate 1/3 ML for the $\sqrt{3}\times\sqrt{3}$ structure. All the ARPES spectra have been obtained by varying the polar angles at a step of 2° along the high symmetry azimuths of the irreducible part of the 1×1 SBZ [see Fig. 1(d)].

In order to explain our experimental results, we have performed DFT total energy calculations for an optimum atomic arrangement of the Tl/Si(111)-1×1 surface. We have also calculated electronic structure of the surface to find surface electronic bands. We have used the local-density approximation for the exchange–correlation functional and norm-conserving, fully separable pseudopotentials. The 5d states of Tl were treated as valence states, and the electronic wave functions were expanded in a plane-wave basis set with a large cutoff energy of 40 Ry. We used a FHI96MD package[6] for the calculations. To test the accuracy of the Tl pseudopotentials, we have calculated the ground state properties of a bulk hcp Tl. This treatment gives lattice constants $a_0 = 3.42$ Å and $c = 5.44$ Å, and a bulk modulus of $B_0 = 42$ GPa. The agreement with experimental data ($a_0 = 3.46$ Å, $c = 5.52$ Å, and $B_0 = 43$ GPa) is good.[7]

The Tl/Si(111)-1×1 surfaces were simulated by using a supercell geometry. We used a repeating slab structure consisting of one Tl layer and eight Si layers with an 8.0 Å vacuum region and a 1×1 surface unit cell. The bottom-layer Si atoms of the slab were terminated by hydrogen atoms. We relaxed all atoms in the slab except for the bottommost Si and H atoms. Geometry optimization was terminated when the remaining forces were smaller than 0.05 eV/Å. Convergence was tested for various adsorption structures and the plane wave cutoff energy of 40 Ry yielded good convergence of structural energy differences.

Figure 1(a) shows the well-known 7×7 LEED pattern obtained from the clean Si(111) surface at room temperature. With the adsorption of Tl, two ordered surfaces of $\sqrt{3}\times\sqrt{3}$ and 1×1 structures appear as presented in Figs. 1(b) and 1(c) at Tl coverages of 1/3 ML and 1.0 ML, respectively. These surfaces are well ordered as indicated by the remarkably dark background. The presence of the $\sqrt{3}\times\sqrt{3}$ surface observed for the first time in this work is in sharp contrast with previous studies reporting the 1×1 surface as the only ordered Tl overlayer structure on the Si(111) surface. Our observation of the $\sqrt{3}\times\sqrt{3}$ structure therefore challenges all the previous claim of considering Tl as an exception among the group III elements exhibiting a so-called "inert pair effect."[2–4] In other words, Tl is just one of typical group III elements including Al, Ga, and In that form a $\sqrt{3}\times\sqrt{3}$ ordered structure at 1/3 ML on the Si(111)-7×7 surface.

In order to identify the binding sites for Tl on the Tl/Si(111)-1×1 surface at 1.0 ML, we have performed total energy calculations for three high-symmetry binding sites T_1, H_3, and T_4 depicted in Fig. 2(a). Interestingly, we find that the sites T_4 and H_3 are more stable than the site T_1 which was suggested as the most stable site by Ricart *et al.* through *ab initio* Hartree–Fock cluster calculations.[3] Moreover the fourfold T_4 site turns out to be slightly more stable than the threefold H_3 site by 0.1 eV. The T_4 site as the binding site for the Tl/Si(111)-1×1 surface is further favored by the LEED I(V) analysis.[8] Detailed bonding geometry with Tl atoms at the T_4 sites is depicted in Fig. 2(b) together with the bonding distances between the neighboring atoms. It is noted that the surface Si atoms are slightly pulled up by the adsorption of the Tl adatoms in this configuration and thereby the bonding between the Si atoms 2 and 3 becomes slightly weakened. We, in fact, observe slight elongations of the atomic distance d_{23} by 0.03 Å and of the height for the Si atom 2 by 0.09 Å in comparison to the corresponding values of the clean bulk-truncated surface.

In order to determine surface bands of the Tl/Si(111)-1×1 surface, we have obtained a series of angle-resolved photoemission spectra along several high symmetry azimuths of the irreducible 1×1 SBZ. A set of such spectra obtained along the $[\bar{1}01]$ direction (or $\bar{\Gamma}$–$\bar{K}$ azimuth) is presented in Fig. 3. The spectra were collected with the incidence angle of photons of energy 21.2 eV fixed at 45°. All the spectra have been normalized by the incident photon flux in order to determine the variation of peak intensity as the exit angle varies. One easily notices that a Tl-derived state (denoted as S_1) disperses significantly as the exit angle of photoelectrons (or equivalently the component $k_\parallel$ of electron momentum parallel to the surface) changes. We present the surface band determined from the ARPES spectra into a gray-scale E_B-$k_\parallel$ diagram in Fig. 4. One finds that the Tl-derived state becomes enhanced in intensity as it approaches towards the zone boundaries whereas it is relatively weak at the zone center ($\bar{\Gamma}$). Note also that it remains almost flat along the $\bar{K}$–$\bar{M}$ azimuth while it disperses significantly as it moves away from the zone center.

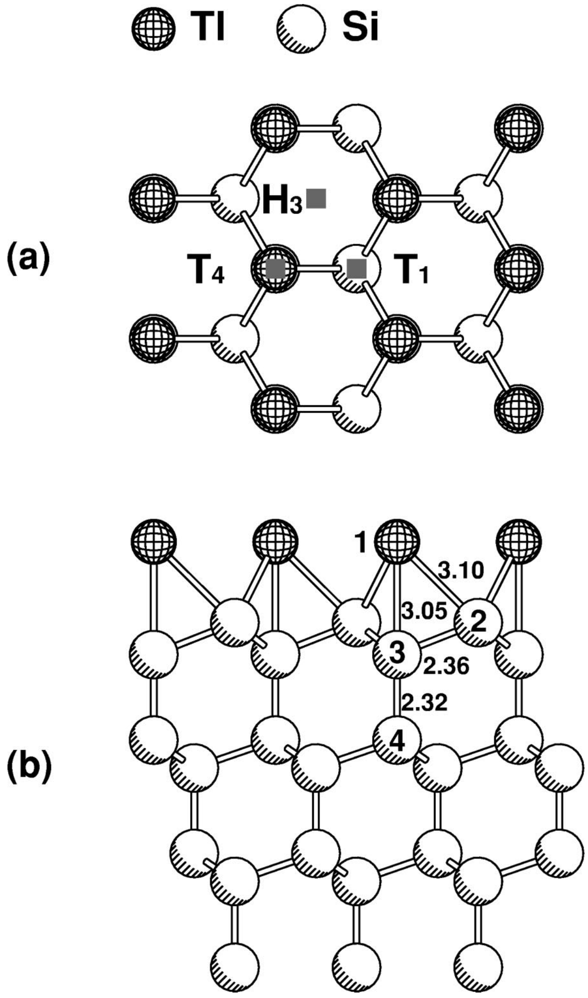

FIG. 2. Geometry-optimized structure of the Tl/Si(111)-1×1 surface at 1.0 ML with Tl at the T_4 sites. Other high symmetry sites such as T_1 and H_3 shown in the top view (a) are found to be less favorable. The numbers in the side view (b) denote the bonding distances in Å between the neighboring atoms. Note the slight variation of the bond lengths induced by Tl compared to the value of 2.33 Å for a bulk Si.

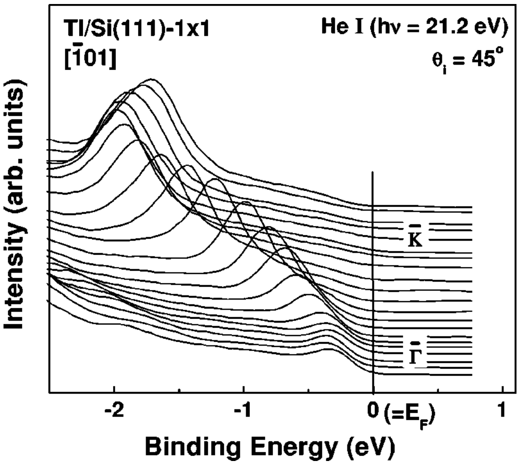

FIG. 3. ARPES spectra collected from the Tl/Si(111)-1×1 surface along the $\bar{\Gamma}$–$\bar{K}$ (or the $[\bar{1}01]$ direction) azimuth. One notes a significantly dispersive band near the Fermi level, which turns out to be a surface band. Similar spectra along the other high symmetric directions are also collected. The incident angle (θ_i) of the photon beam is fixed at 45°.

Since the only surface state near the Fermi level S_1 does not cross the Fermi level throughout the SBZ, and the 1×1 unit cell at 1.0 ML has an even number of electrons, the Tl-induced 1×1 surface can be safely considered as a band insulator in the scheme of a single electron band theory. The fact that this surface is extremely inert to foreign adsorbates such as oxygen atoms reflects the electronically saturated nature of the surface dangling bonds. More specifically the dangling bonds of three surface Si atoms associated with a T_4 site become saturated by the three electrons transferred from the Tl adatom.

Our calculated band structure for the geometry optimized Tl/Si(111)-1×1 surface is presented in Fig. 4(b). Here we find two distinct surface bands; one filled S_1 band and another empty S_2 band above Fermi level. Not only the fact that the surface is semiconducting but also the energy-momentum dispersion relation of the S_1 band are well reproduced in our calculations. The band maximum of the filled S_1 band is located at the $\bar{\Gamma}$ point whereas the band minimum of the empty S_2 band occurs at the $\bar{K}$ point from which we obtain the band gap of 0.34 eV. Although the origin of the semiconducting nature of the Tl/Si(111)-1×1 surface is briefly stated above as the saturation of all the dangling bonds, the charge redistribution due to the adsorption of Tl atoms appearing in Fig. 5(a) as the contour plot of the charges of the S_1 band explicitly supports our earlier explanation.

The state S_1 apparently represents the saturated dangling-bond state of Si atom 2. By contrast, the charges of the empty surface state S_2 are localized mostly around the H_3 sites as shown in Fig. 5(b). Figure 5(c) shows the distribution of the difference in charge density of the Tl/Si(111)-1×1 surface. It was obtained by subtracting the sum of the charge densities of the isolated Tl layer and the Si substrate from that of the Tl/Si(111)-1×1 surface. It is noted that the charges are transferred from the Tl adatoms partially to Si atom 2 to saturate the surface Si dangling bonds. We also find the enhanced charges of a p_z orbital character between Si atoms 3 and 4. Based on these observations, we are led to conclude that the bonding of Tl adatoms on the Si(111)-1×1 surface is mainly ionic and that all the Si dangling bonds are saturated by the electrons transferred from Tl adatoms to make the surface semiconducting.

We have studied the adsorption of Tl on the Si(111)-7×7 surface. The observation of a stable well-defined $\sqrt{3}\times\sqrt{3}$ overlayer structure at 1/3 ML denies the "inert pair effect" attributed only to Tl among group III elements. The unique surface band found in our ARPES measurements from the Tl/Si(111)-1×1 surface at 1.0 ML shows that the surface is semiconducting. Our DFT calculations reproduce the surface band quite well. It stems from the dangling bonds of the surface Si atoms saturated by electrons transferred from the Tl adatoms. The saturation of the surface dangling bonds makes the Tl/Si(111)-1×1 surface extremely inert to

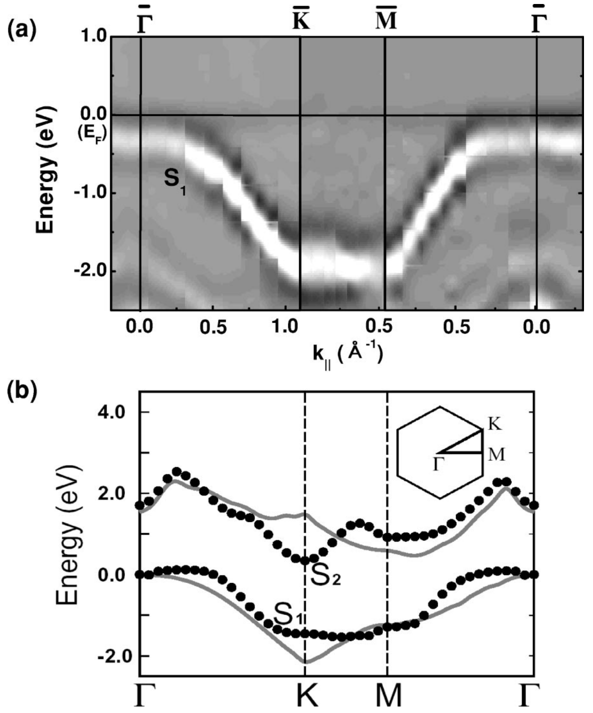

FIG. 4. (a) Experimental energy-momentum (the component parallel to surface $k_{\|}$) dispersion relation of the Tl/Si(111)-1×1 surface determined from the ARPES spectra for the irreducible SBZ. The brightness at a given $k_{\|}$ is proportional to the spectral intensity of the state. This observed filled surface band is well reproduced in our calculated band structure of the surface (b) with Tl at the $\underline{T_4}$ sites. Energy is referenced to the valence band maximum at the $\bar{\Gamma}$. Edges of the projected bulk band structure are denoted by gray solid curves. The two surface states, one filled band S_1 and another empty S_2 denoted with solid circles appear in the bulk gap. One finds a band gap of 0.34 eV between the maximum of the S_1 and the minimum of the S_2 band. Inset shows the surface Brillouin zone of the 1×1 unit cell.

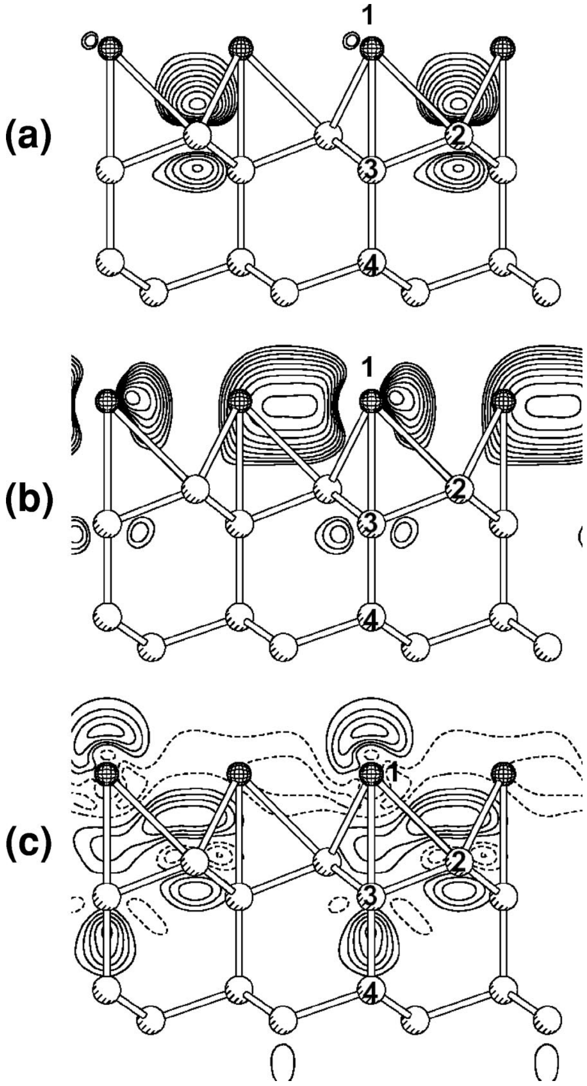

FIG. 5. Charge density contours of the filled surface state S_1 (a) and the empty state S_2 (b) at the $\bar{K}$ point of the Tl/Si(111)-1×1 surface. A contour plot of the charge-density difference between the Tl/Si(111)-1×1 surface and the isolated Tl layer plus the Si surface (c). Solid and dashed curves represent increased and decreased regions of charge density, respectively.

foreign adsorbates. Our calculations further show that the surface is a band insulator with a band gap of 0.34 eV.

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*Electronic address: jwc@postech.ac.kr; URL:http://www.postech.ac.kr/phys/snpl/

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