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Core-level photoemission study of thallium adsorbed on a Si(111)-(7×7) surface: Valence state of thallium and the charge state of surface Si atoms

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The coverage-dependent valence state of Tl adsorbed on a Si(111)-(7×7) surface and the coverage dependence of the charge states of surface Si atoms have been investigated by high-resolution core-level photoelectron spectroscopy. Although two different reconstructions were observed in low-energy electron diffraction at different coverages, a (1×1) pattern at a Tl coverage of 1 monolayer (ML) and a ($\sqrt{3}\times\sqrt{3}$) pattern at a coverage of 1/3 ML, the binding energy of the Tl 5*d* core-level was the same at Tl coverages up to 1 ML. Taking the valence state on a (1×1) surface reported in the literature into account, we conclude that the valence state of Tl is 1+, and that the $6s^2$ electrons of Tl are inactive as an inert pair in the Tl-Si bonding on a Si(111) surface at a coverage of 1 ML and below. In the Si 2*p* core-level spectra, one surface component was observed on the (1×1) surface, and three surface components were observed on the ($\sqrt{3}\times\sqrt{3}$) surface. The binding energies and intensities of the Si 2*p* surface components indicate that the charge state of the surface Si atoms on Tl/Si(111)-(1×1) is the same as that of the ($\sqrt{3}\times\sqrt{3}$) surfaces induced by the other group III metals, but they are different on the Tl/Si(111)-($\sqrt{3}\times\sqrt{3}$) surface.

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I. INTRODUCTION

Motivated by the technological importance of nanometer-scale electronic devices, self-assembling one-dimensional and two-dimensional superstructures, formed on semiconductor surfaces by the adsorption of metal atoms, are of increasing interest. From a scientific point of view, these one- and two-dimensional structures have attracted much attention due to the possibility of observing various exotic low-dimensional physical phenomena.[1,2] The low-dimensional structures formed by the adsorption of group III metals on semiconductor surfaces are candidates for such systems. So far, numerous studies have been performed on the interaction between the metals Al, Ga, and In in group III and Si surfaces. On a Si(111)-(7×7) surface, these three group III metals have been reported to form common surface structures such as magic cluster arrays at modest temperature,[3–7] and a ($\sqrt{3}\times\sqrt{3}$) reconstruction [Fig. 1(a)] with an adsorbate coverage of 1/3 monolayer (ML) at higher temperatures.[8–12]

Recently, the study on group III metals on Si(111)-(7×7) has been expanded to the heaviest element of this group, thallium (Tl), whose behavior differs from those of the lighter group III metals (Al, Ga, and In), i.e., Tl has a peculiar behavior in the form of the so-called "inert pair effect." In fact, the adsorption of Tl on Si(111)-(7×7) has been reported to form a (1×1) phase at a coverage of 1 ML.[13–18] This phase has not been observed by the adsorption of other group III metals. On the (1×1) surface, Tl atoms are adsorbed on the T_4 sites of the bulk terminated unreconstructed Si(111) surface[16–18] as shown in Fig. 1(b), and the $6s^2$ electrons of Tl have been reported to be inactive as an inert pair in the Tl-Si bonding.[16,18] This means that Tl behaves as a monovalent atom on the (1×1) surface. Together with the well-ordered (1×1) surface, small (3×1) and ($\sqrt{3}\times\sqrt{3}$) domains have been observed using scanning tunneling microscopy (STM) depending on the adsorption conditions.[15] The (3×1) reconstruction is a typical phase formed by monovalent atoms (alkali metals or Ag) at a coverage of 1/3 ML, and the ($\sqrt{3}\times\sqrt{3}$) reconstruction is a typical phase formed by the other group III trivalent atoms at a coverage of 1/3 ML. Based on the observation of these three phases a variable valency for Tl on a Si(111) surface has been proposed.[15,16] However, so far, there is no investigation on the valence state of Tl on a Si(111) surface, and therefore no strong evidence on the variable valence of Tl.

In this paper, we present a high-resolution core-level photoelectron spectroscopy study performed to determine the coverage-dependent valence state of Tl adsorbed on a Si(111)-(7×7) surface and the charge states of surface Si atoms. In the low-energy electron diffraction (LEED) study, a (1×1) pattern was observed at a Tl coverage of 1 ML and a ($\sqrt{3}\times\sqrt{3}$) pattern was observed at a coverage of 1/3 ML.

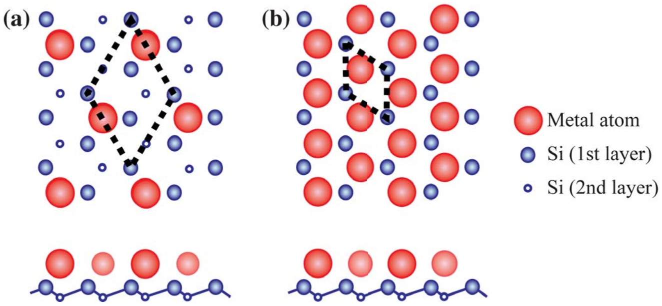

FIG. 1. (Color online) Schematic illustrations of (a) a group III metal induced Si(111)-($\sqrt{3}\times\sqrt{3}$) surface, and (b) the Si(111)-(1×1) surface formed by the adsorption of 1 ML of Tl. Large filled circles are metal atoms, which are adsorbed on the T_4 site, and the other circles are Si atoms. The thick dashed lines indicate the unit cell of each surface.

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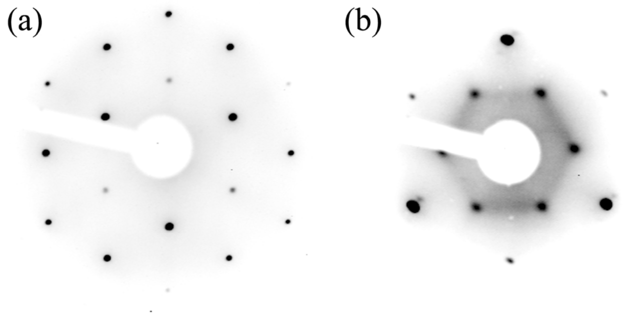

FIG. 2. LEED patterns of (a) the Tl/Si(111)-(1×1) surface and (b) the Tl/Si(111)-$(\sqrt{3}\times\sqrt{3})$ surface. The primary electron energies are (a) 53 eV and (b) 43 eV.

The binding energy of the Tl 5*d* core level was the same not only at these two coverages but also at coverages up to 1 ML. This result indicates that the valence state of Tl is constant at coverages of 1 ML and below. In the Si 2*p* core-level spectra, one surface component was observed on the (1×1) surface, and three surface components on the $(\sqrt{3}\times\sqrt{3})$ surface. The binding energy and intensity of the Si 2*p* surface component indicate that the charge states of the surface Si atoms are almost the same on the Tl induced (1×1) surface and on the Al, Ga, and In induced $(\sqrt{3}\times\sqrt{3})$ surfaces. Regarding the Tl induced $(\sqrt{3}\times\sqrt{3})$ surface, the Si 2*p* core-level spectra indicate that the charge states of the surface Si atoms are different from those of other group III metal induced $(\sqrt{3}\times\sqrt{3})$ surfaces.

II. EXPERIMENTAL DETAILS

The high-resolution photoemission measurements were performed at beamline 33 at the MAX-I synchrotron radiation facility in Lund, Sweden. The Tl 5*d* and Si 2*p* core-level spectra were obtained with an angle-resolved photoelectron spectrometer with an angular resolution of ±2°. The total experimental energy resolutions were ~180 meV for the Tl 5*d* measurements and ~80 meV for the Si 2*p* measurements. The Si(111) sample, cut from an Sb-doped (*n*-type, 3 Ω cm) Si wafer, was preoxidized chemically before it was inserted into the vacuum system. In order to obtain a clean surface, we annealed the sample at 1230 K by direct resistive heating in the vacuum chamber to remove the oxide layer, and at 1520 K to remove carbon contamination from the surface. After the annealing, a sharp (7×7) LEED pattern was observed, and neither the valence-band spectra nor the Si 2*p* core-level spectra showed any indication of contamination. Thallium was deposited from a Knudsen cell onto a clean Si(111)-(7×7) surface at a substrate temperature of 570 K. The base pressure was below 4×10^{-11} Torr during the measurements, and below 1×10^{-10} Torr during the Tl evaporation.

III. RESULTS AND DISCUSSION

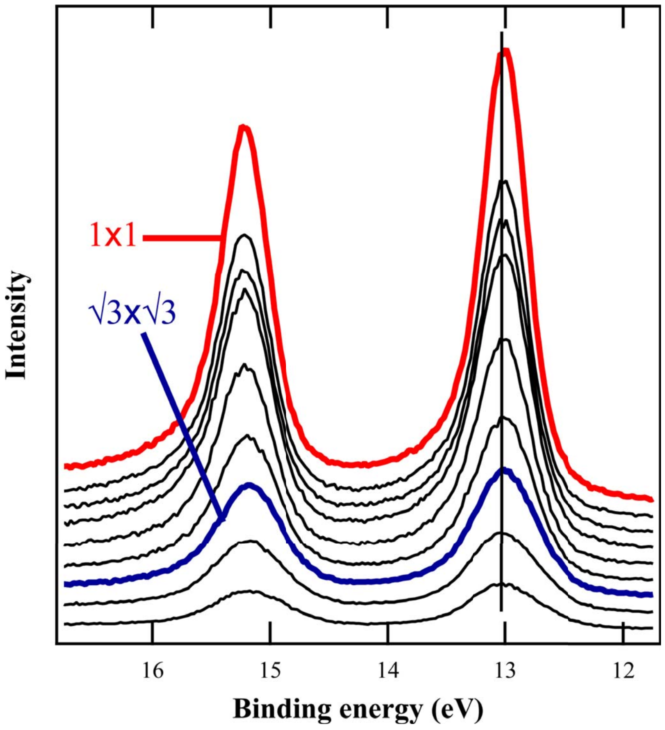

FIG. 3. (Color online) Coverage-dependent Tl 5*d* core-level spectra obtained with a photon energy of 50 eV. The uppermost spectrum is the Tl 5*d* core level of the highest coverage (1×1) surface, and Tl coverage decreases as going downward. The third spectrum from the bottom is the Tl 5*d* core level of the $(\sqrt{3}\times\sqrt{3})$ surface.

Figure 2(a) shows the LEED pattern of the Tl/Si(111)-(1×1) surface obtained at a Tl coverage of 1.0 ML with a primary electron energy of 53 eV. Only strong and sharp ×1 spots are observed with a remarkably low background intensity, and thus this pattern warrants the high quality of the (1×1) surface used in the present study. The LEED pattern shown in Fig. 2(b) was obtained by reducing the Tl coverage by annealing the Tl/Si(111)-(1×1) surface at a temperature between 600 and 650 K. The primary electron energy used in Fig. 2(b) was 43 eV. Although the background intensity is slightly higher than that in Fig. 2(a), the strong $\times\sqrt{3}$ spots observed in Fig. 2(b) indicate the formation of a surface covered almost entirely with $(\sqrt{3}\times\sqrt{3})$ domains, instead of small domains as reported by STM.[15] The formation of a well-defined Tl induced $(\sqrt{3}\times\sqrt{3})$ surface was also observed in a recent LEED study.[16]

Figure 3 shows Tl 5*d* core-level spectra obtained at different Tl coverage with a photon energy ($h\nu$) of 50 eV and an emission angle (θ_e) of 0°, i.e., normal emission. The Tl 5*d* core-level spectra were normalized using the background intensity, which is proportional to the photon flux. The uppermost spectrum shows the Tl 5*d* core-level emission of the Tl/Si(111)-(1×1) surface with a coverage of 1.0 ML, and the spectra below were obtained by reducing the Tl coverage by annealing the (1×1) surface at temperatures between 600 and 700 K. The third spectrum from the bottom is the Tl 5*d* core-level spectrum of the $(\sqrt{3}\times\sqrt{3})$ surface shown in Fig. 2(b). Based on the Tl coverage of the (1×1) surface and the fact that the intensity of the $(\sqrt{3}\times\sqrt{3})$ spectrum is 1/3 of the (1×1) spectrum, we conclude that the Tl coverage of the

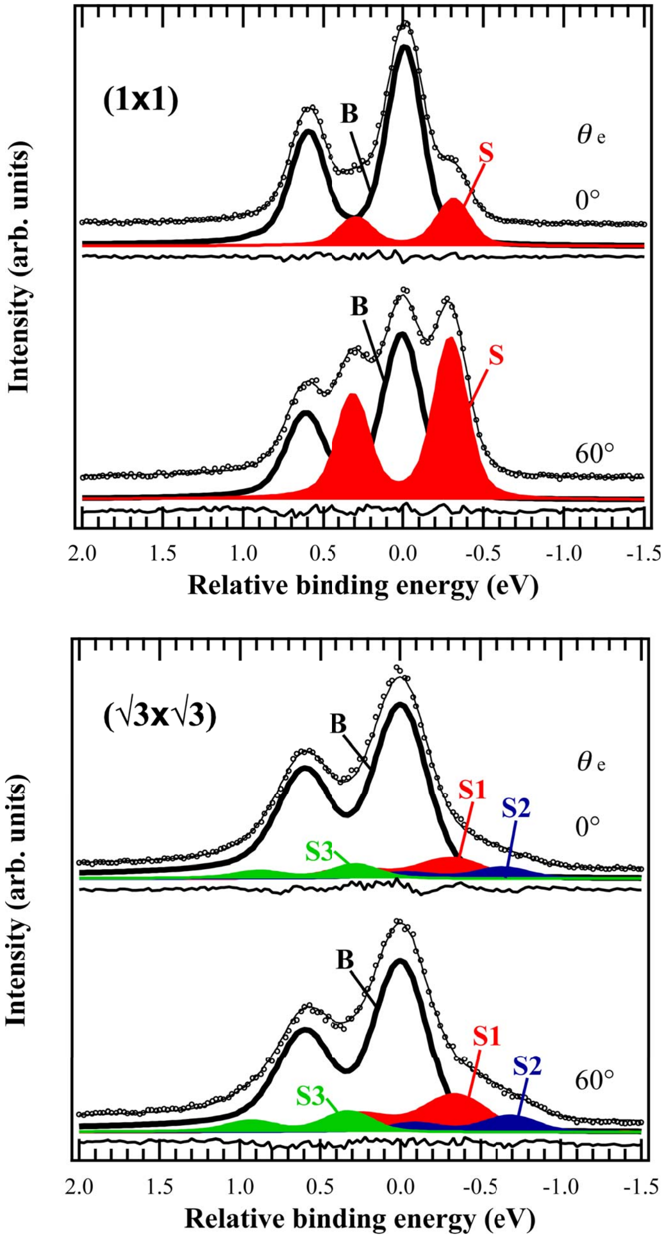

FIG. 4. (Color online) Si $2p$ core-level spectra of the Tl/Si(111)-(1×1) and $(\sqrt{3}\times\sqrt{3})$ surfaces measured with $h\nu=135$ eV at $\theta_e=0°$ and 60°. The open circles are the experimental data, and the solid lines overlapping the open circles are the fitting curves. Each component is indicated by different shading. The difference between the experimental data and fitting result is shown by a solid line at the bottom of each spectrum.

$(\sqrt{3}\times\sqrt{3})$ surface is 1/3 ML. As shown in Fig. 3, the Tl $5d_{5/2}$ and $5d_{3/2}$ core levels are observed at binding energies of approximately 13 and 15.2 eV in the spectrum of the (1×1) surface, and they do not shift as the Tl coverage decreases.[19] Further, no structure except these two peaks is observed in any of the spectra. Taking into account that the difference in binding energies of the $5d$ core levels for the Tl^{1+} and Tl^{3+} is reported to be 0.58 eV,[20] the result shown in Fig. 3 indicates that the valence state of Tl is identical in the coverage range investigated in the present study. Therefore, based on the valence state of Tl on the (1×1) surface reported in previous studies,[16,18] we conclude that the valence state of Tl is 1+ and thus the $6s^2$ electrons of Tl are inactive as an inert pair in the Tl-Si bonding on a Si(111) surface at coverages up to 1 ML. The core-level result is not consistent with the variable valency of Tl on Si(111) proposed in the literature.

In order to obtain more detailed information about the Tl/Si(111)-(1×1) and $(\sqrt{3}\times\sqrt{3})$ surfaces, we have measured the Si $2p$ core-level spectra of these two surfaces. Figure 4 shows the results obtained with $h\nu=135$ eV at two different emission angles (θ_e) that give a difference in the surface sensitivity. Without any processing, the experimental spectra (open circles) of the (1×1) surface reveal the presence of one surface component that contributes to the shape of the spectra. That is, both the Si $2p_{3/2}$ and $2p_{1/2}$ components of S are observed as peaks in the spectrum obtained using $\theta_e=60°$, and the Si $2p_{3/2}$ component of S is clearly observed as a shoulder in the spectrum obtained using $\theta_e=0°$. Concerning the $(\sqrt{3}\times\sqrt{3})$ surface, the broad spectral feature and the presence of the long tails on both the high and low energy sides of the main peak suggest that the number of surface components of the $(\sqrt{3}\times\sqrt{3})$ surface is larger than that of the (1×1) surface.

Quantitative information about the components that contribute to the shape of the spectra is obtained by analyzing the Si $2p$ spectra by a standard least-squares-fitting method using spin-orbit split Voigt functions. The solid lines overlapping the data in Fig. 4 are the fitting curves. We used 608 meV for the spin-orbit splitting and an 80 meV full width at half maximum (FWHM) for the Lorentzian contribution for all components in the fitting procedure. The Gaussian width of the bulk component is 210 meV (FWHM) in the spectra of the (1×1) surface, and 335 meV (FWHM) in those of the $(\sqrt{3}\times\sqrt{3})$ surface. The Gaussian width of the surface component is 195 meV on the (1×1) surface, and the widths of the surface components are between 335 and 400 meV on the $(\sqrt{3}\times\sqrt{3})$ surface. A polynomial background was subtracted before the decomposition of each spectrum, and each component is indicated by different shading. The difference between the experimental data and fitting result is indicated by a solid line at the bottom of each spectrum.

From the result of the fitting procedure, we can conclude that the (1×1) surface has one surface component and the $(\sqrt{3}\times\sqrt{3})$ surface has at least three surface components. Among the surface components, the S component of the (1×1) surface and the S1 component of the $(\sqrt{3}\times\sqrt{3})$ surface are observed at the same relative binding energy, i.e., the binding energy of S and S1 are −300 meV relative to the B component. The relative binding energies of the S2 and S3 components, which are observed on the $(\sqrt{3}\times\sqrt{3})$ surface, are −630 and 285 meV. The intensity ratio of the B and S components is approximately 1:0.91 at $\theta_e=60°$, and approximately 1:0.24 at $\theta_e=0°$ on the (1×1) surface. On the $(\sqrt{3}\times\sqrt{3})$ surface, the intensities of S1, S2, and S3 relative to the bulk one are 0.25, 0.09, and 0.11 at $\theta_e=60°$, and 0.10, 0.06, and 0.07 at $\theta_e=0°$.

By comparing the Si $2p$ core-level spectra of the Al, Ga, and In induced Si(111)-$(\sqrt{3}\times\sqrt{3})$ surfaces[21–25] and the results shown in Fig. 4, one notices that the spectral shapes and the fitting results of the Tl/Si(111)-(1×1) surface closely resemble those of the $(\sqrt{3}\times\sqrt{3})$ surfaces induced by the other group III metals. That is, a surface component, whose relative binding energy is similar to that observed in Fig. 4 is observed on the Al, Ga, and In induced Si(111)-$(\sqrt{3}\times\sqrt{3})$ surfaces. The origin of the surface component of Al, Ga, and In induced $(\sqrt{3}\times\sqrt{3})$ has been reported to be the first layer Si atoms that are negatively charged due to charge transfer from metal atoms. Since the unreconstructed Si(111)-(1×1) structure is common to both the Tl/Si(111)-(1×1) surface and the other group III metal induced $(\sqrt{3}\times\sqrt{3})$ surfaces (the only difference in structure is the adsorbate coverage), the similarity in binding energies of the surface components suggests that the charge states of the first layer Si atoms are almost the same on these surfaces. On the unreconstructed Si(111)-(1×1) clean surface, the high density of half-filled dangling bonds makes this surface unstable (there is one dangling bond per one surface Si atom). The charge transfer from metal atoms might be the origin of the stabilization of the unreconstructed Si(111)-(1×1) structure underneath the group III metal overlayer.[26] A semiquantitative correlation between the charge transfer and the adsorbate-induced core-level shifts has been derived empirically for the Si $2p$ core level as $\delta E/A$ eV$=\delta q$,[27,28] where A is a constant with a value between 2 and 3.4, δq is the charge transfer, and δE is the core level shift. Taking this relation and the relative binding energies of the surface components into account, we propose that a charge transfer of approximately 0.1 electron per surface Si atom stabilizes the unreconstructed Si(111)-(1×1) structure on which the group III metal atoms are located.

Regarding the Tl/Si(111)-$(\sqrt{3}\times\sqrt{3})$ surface, the core-level result is completely different from that of the trivalent Al, Ga, or In atoms induced $(\sqrt{3}\times\sqrt{3})$ surface. This result supports that the valence state of Tl on a Si(111)-$(\sqrt{3}\times\sqrt{3})$ surface is +1, a value that is different from the valence state of the other group III metal atoms. The relative binding energy of the S1 component is the same as that of the S component, but the relative intensity of S1 is approximately 1/3 of that of S. Based on this result and the 1+ valence state of Tl at a coverage of 1/3 ML, we conclude that Tl atoms affect only 1/3 of the first layer Si atoms on the $(\sqrt{3}\times\sqrt{3})$ surface. However, although two dangling bonds per unit cell are expected to remain on the surface, the Tl/Si(111)-$(\sqrt{3}\times\sqrt{3})$ surface is quite stable. A $(\sqrt{3}\times\sqrt{3})$ LEED pattern and Si $2p$ core-level spectra with the same qualities as those shown in Figs. 2 and 4 were observed more than 12 h after the sample preparation. One of the origins for this stability might be the charge distribution in the surface layer of Tl/Si(111)-$(\sqrt{3}\times\sqrt{3})$ that is different from those of the trivalent metal induced $(\sqrt{3}\times\sqrt{3})$ surfaces. The difference in charge distribution, which is obvious from the presence of the two additional surface components (S2 and S3) and their binding energies, suggests that the charge transfer between surface Si atoms might lead to a removal of dangling bonds.[29] We propose that the charge redistribution in the Si surface layer contributes to the stability of the monovalent Tl induced Si(111)-$(\sqrt{3}\times\sqrt{3})$ surface.

IV. CONCLUSION

In conclusion, we have investigated the coverage-dependence of the valence state of Tl adsorbed on a Si(111)-(7×7) surface and the charge states of surface Si atoms by high-resolution core-level photoelectron spectroscopy. The binding energy of the Tl $5d$ core level of the (1×1) surface obtained at a Tl coverage of 1 ML was the same as that of the $(\sqrt{3}\times\sqrt{3})$ surface obtained at a coverage of 1/3 ML. Taking into account that the binding energy of the Tl $5d$ core level was the same at not only these two coverages but at coverages up to 1 ML, we conclude that the valence state of Tl is +1 in this coverage range. This means that the $6s^2$ electrons of Tl are inactive as an inert pair in the Tl-Si bonding on a Si(111) surface for coverages up to 1 ML, and thus that there is no variable valency for Tl on a Si(111) surface. Regarding the Si $2p$ core-level spectra, one surface component was observed on the (1×1) surface. By comparing the binding energy and intensity of this surface component with those of the surface components of the Al/,Ga/, and In/Si(111)-$(\sqrt{3}\times\sqrt{3})$ surfaces, the origin of this component is concluded to be the surface Si atoms that are negatively charged due to charge transfer from Tl atoms. Further, the quite similar binding energies of the surface components suggest that the charge states of the first layer Si atoms are almost the same on the Tl/Si(111)-(1×1) and Al/, Ga/, and In/Si(111)-$(\sqrt{3}\times\sqrt{3})$ surfaces. Based on a semiquantitative correlation between the charge transfer and the adsorbate-induced core-level shifts, we propose that a charge transfer of approximately 0.1 electron per surface Si atom stabilizes the unreconstructed Si(111)-(1×1) structure underneath the group III metal overlayers. On the Tl/Si(111)-$(\sqrt{3}\times\sqrt{3})$ surface, three surface components were observed in the Si $2p$ core-level spectra. The binding energies and relative intensities of these surface components indicate that the charge distribution in the surface Si layer on Tl/Si(111)-$(\sqrt{3}\times\sqrt{3})$ is different from that on the other group III metal induced $(\sqrt{3}\times\sqrt{3})$ surfaces.

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[26] Not only the group III metals, but also the group IV metals (Sn and Pb) induced Si(111)-$(\sqrt{3}\times\sqrt{3})$ surfaces show a surface component with a quite similar relative binding energy. The basic structure of the uppermost Si layer of the group IV metal (Sn and Pb) induced $(\sqrt{3}\times\sqrt{3})$ surfaces is (1×1). Thus the similarity in binding energy supports our proposition that the amount of charge transfer, which contributes to the stability of the Si(111)-(1×1) structure, has little relation to the actual species adsorbed.

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[29] Charge transfer between surface Si atoms can result from the formation of Si dimers or from the presence of Si adatoms, suggesting that the outermost Si atoms of the $(\sqrt{3}\times\sqrt{3})$ surface do no longer follow the unreconstructed Si(111)-(1×1) structure.