PHYSICAL REVIEW B **69**, 195311 (2004)

Structural properties of a thallium-induced Si(111)-1×1 surface

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(Received 27 March 2003; revised manuscript received 20 January 2004; published 25 May 2004)

We report on the atomic arrangement of a thallium (Tl) induced 1×1 phase on a Si(111) surface determined by utilizing synchrotron x-ray scattering. Based on a quantitative analysis of intensity profiles of several crystal truncation rods, we find that Tl adatoms occupy the T_4 sites to produce a significantly asymmetric bonding geometry with neighboring Si atoms in the first silicon bilayer. The atomic arrangement determined in this study, including the bond length of 3.26 ± 0.02 Å for the Tl-Si bonds, agrees quite well with the one reported earlier. Our results not only provide bonding parameters of the surface with an improved accuracy, but also confirm the theoretical prediction that the Tl-Si bonding is more ionic than covalent.

DOI: 10.1103/PhysRevB.69.195311 PACS number(s): 61.10.Nz, 68.43.Fg, 68.47.Fg, 68.18.Jk

The interaction between metallic adatoms and semiconducting surfaces has been a subject of extensive research effort mostly due to its wide applications in the semiconductor industry as well as growing academic interest. Such an endeavor is basically an attempt to understand some novel surface/interface phenomena, including adsorbate-induced reconstruction of a substrate surface and the subsequent changes in its physical properties. The adsorption of thallium (Tl) on the Si(111)-7×7 surface, in particular, has attracted attention due to its peculiar behavior in the form of the so-called "inert pair effect," which sets it apart from that of other group III metallic elements such as Al, Ga, and In.[1–3] The $6s^2$ electrons of Tl have been considered inactive as an inert pair in the Tl-Si bonding in order to explain the presence of a 1×1 phase at 1.0 monolayer (ML) as the only ordered phase [1 ML corresponds to the atomic density in the top layer of the unreconstructed Si(111) surface, i.e., 7.83×10^{14} atoms cm^{-2}]. Tl atoms of the 1×1 phase are, therefore, thought to behave as monovalent atoms. This feature is in sharp contrast with the trivalent nature found in the $\sqrt{3} \times \sqrt{3}$ phase observed commonly in all other group III elements on the Si(111) surface. Earlier studies thus claimed that Tl atoms occupied T_1 sites directly on top of the unreconstructed Si layer due to the monovalent character of Tl atoms.[4–7] This "inert pair effect," however, has been challenged both experimentally by observing a stable Tl-induced $\sqrt{3} \times \sqrt{3}$ phase and theoretically by finding a T_4 site as the most stable binding site for Tl atoms in the Tl-induced 1×1 surface.[8] The T_4 sites for Tl have been further confirmed by recent low-energy electron diffraction (LEED) $I(V)$ analysis.[9] Interestingly, Kotlyar *et al.* have also reported that Tl adatoms display a variable valency by observing a new 3×1 phase as well as a $\sqrt{3} \times \sqrt{3}$ phase by scanning-tunneling microscopy (STM).[10]

Despite the atomic models already reported for the Tl-induced 1×1 surface,[8,9] we have attempted to determine the atomic arrangement more accurately by using synchrotron x-ray diffraction that is not hampered by the multiple scattering effect in LEED measurement. In order to focus our effort on the determination of the interlayer spacings, we have measured several crystal truncation rods (CTR's) including $(00L)$, $(10L)$, and $(11L)$, where L is the Miller index along the direction normal to the surface. In this paper, we report the atomic arrangement obtained from our CTR data in detail and discuss their physical implications. The atomic structure we present here may serve as a better basis for the improved understanding of physical properties such as the surface electronic band structure reported earlier.[8]

In order to measure diffraction data from the Tl-induced 1×1 surface using synchrotron x rays, a custom-designed ultrahigh-vacuum (UHV) x-ray-scattering chamber with a beryllium window was mounted on a four-circle diffraction goniometer (2+2 mode) at the 5C2 K-JIST beamline of the Pohang Light Source in Korea.[11,12] The incident x rays were vertically focused by a mirror and monochromatized to a wavelength of 1.23 Å by a double-bounce silicon (111) monochromator. This monochromator was also used to focus the beam in the horizontal direction. The momentum transfer resolution was controlled by two pairs of slits mounted on the detector arm. The beam size was $1.0 \times 1.0\ \mathrm{mm}^2$ and the detector slits were set to $1.2 \times 1.2\ \mathrm{mm}^2$, which resulted in a resolution function much less than 0.01 reciprocal-lattice units (r.l.u.) along the truncation rods.

The sample was cut into a size of $8 \times 20 \times 0.3\ \mathrm{mm}^3$ from an n-type Si wafer with a resistivity of 8.0–15.0 Ω cm and mounted inside the UHV scattering chamber. The base pressure of the chamber was maintained below 5×10^{-10} Torr during the entire experiment. The chamber was equipped with a rear-view LEED optics and a Tl metal source. The beryllium window of the scattering chamber allows in-plane and out-of-plane access of 50°. The Si sample was cleaned by repeated degassing at 600 °C with frequent flashings up to 1200 °C followed by annealing at 850 °C. The sample cooled slowly down to room temperature after such a cleaning process produced a well-defined 7×7 LEED pattern, indicating the cleanliness of the surface. We have confirmed

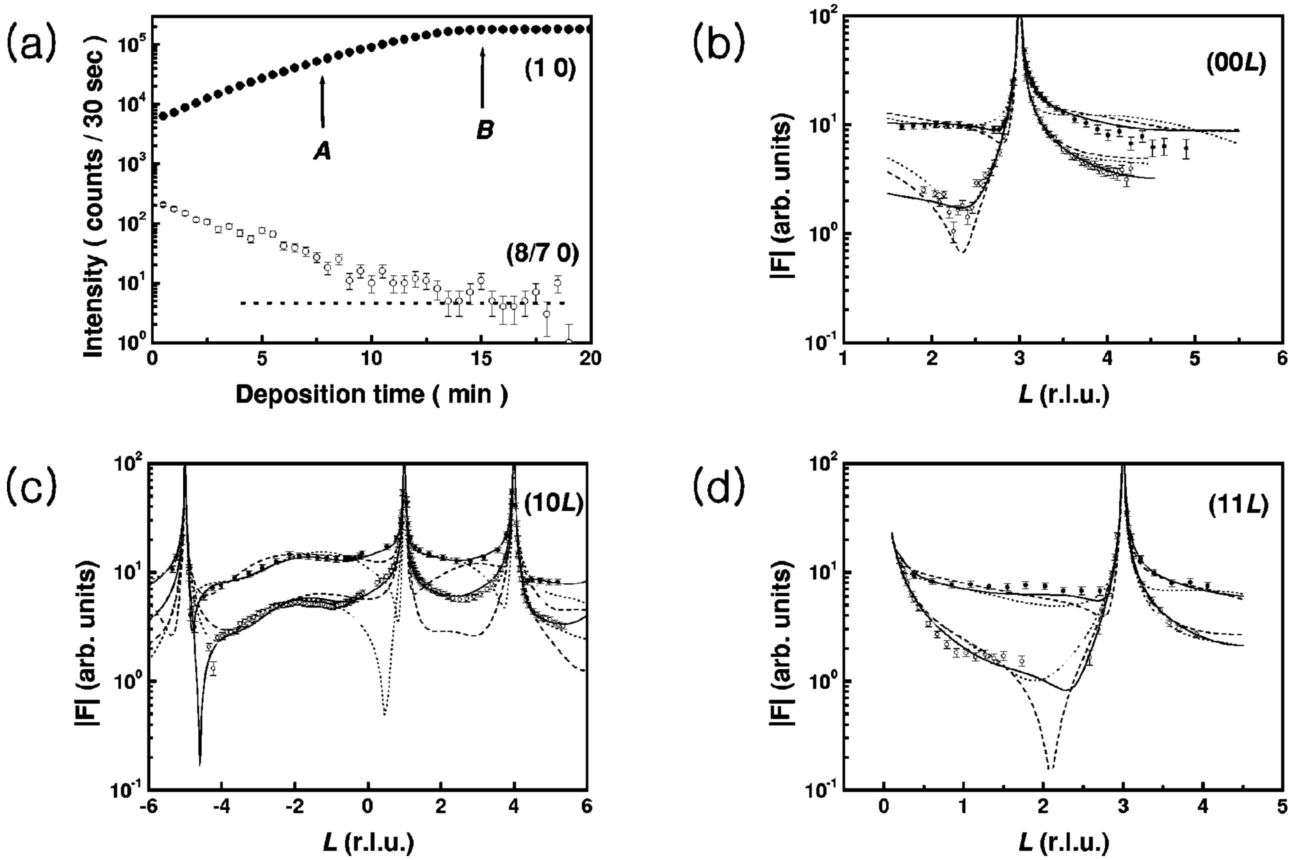

FIG. 1. (a) Development of the Tl-induced 1×1 phase on the Si(111)-7×7 surface as a function of Tl exposure. One finds that the phase grows with Tl exposure and is best developed at 15 min of exposure (denoted as *B*) where the (1 0) spot becomes strongest while fractional-order spots such as the (8/7 0) from the Si substrate disappear completely into the background (horizontal dotted line). The sample has been maintained at ≈300 °C during measurements. (b)–(d) Crystal truncation rods (CTRs) have been measured along the direction normal to the surface from the integer-order spots (0 0), (1 0), and (1 1). The $L<0$ data of the $(10L)$ CTR are obtained by measuring the equivalent reflections $(\bar{1}0\bar{L})$. The scans taken for two different exposures, denoted as *A* (7.5 min) and *B* in (a), are presented as open and filled circles in (b)–(d), respectively. Solid curves are the best fit to the experimental data based on a T_4 model. Calculated CTRs assuming Tl atoms at T_1 sites (T_1 model, dashed) and at H_3 sites (H_3 model, dotted) clearly exhibit significant deviation from experimental data.

the cleanliness of the sample, whenever necessary, by routinely measuring a series of seventh-order spots of the 7×7 surface with grazing-incidence x-ray diffraction.

We adopt a convention for a hexagonal unit cell for the Si(111) surface. Three lattice vectors are $\mathbf{a}_1=\frac{1}{2}[10\bar{1}]$, $\mathbf{a}_2=\frac{1}{2}[\bar{1}10]$, and $\mathbf{a}_3=[111]$. The corresponding reciprocal lattice is formed by $\mathbf{b}_1=\frac{1}{3}[22\bar{4}]$, $\mathbf{b}_2=\frac{1}{3}[\bar{2}4\bar{2}]$, and $\mathbf{b}_3=\frac{1}{3}[111]$. The momentum transfer $\mathbf{Q}$ is characterized by indices (HKL) through $\mathbf{Q}=H\mathbf{b}_1+K\mathbf{b}_2+L\mathbf{b}_3$.

After cleaning the sample by the recipe mentioned above, Tl atoms were then deposited on the clean Si(111)-7×7 surface held at an elevated temperature ≈300 °C. A well-defined Tl-induced 1×1 surface can be identified by the 1×1 LEED pattern with sharp and bright integral-order diffraction spots in a dark background. The surface thus prepared appears to be the best developed one as seen by the saturated intensity of the normal spot (1 0) and the fractional-order (8/7 0) peak, which weakens with increasing Tl content and eventually disappears completely [Fig. 1(a)]. We assign the saturation coverage of Tl as 1.0 ML, which is also verified from the fits discussed below.

Two sets of CTR scans have been taken at two different Tl coverages of 0.5 ML and 1.0 ML marked as *A* and *B*, respectively, in Fig. 1(a). Additionally, 42 symmetry-equivalent reflections have been acquired for CTRs at *A*. Intensity profiles of the CTRs from the 1×1 surface at room temperature have been obtained by integrating a set of ϕ scans at various L values. Similarly integrated intensities have been estimated by integrating the peaks numerically with the background subtracted in a consistent manner. The structure factors shown in Figs. 1(b)–1(d) have been derived from the integrated intensities corrected by Lorentz factor, polarization factor, area correction, and interception of rods.[13] The intensity errors for CTRs at *A* are ~12% due to the counting statistics and the variance of symmetry equivalents.[14] The systematic error has also been applied to other CTRs. The specular rods $(00L)$ obtained by rocking the sample in the scattering plane have been corrected by different correction factors. In the fit, these specular rods have been combined with other integer-order rods by a separate scale factor. All the model calculations and numerical fittings have been performed using a ROD program.[15]

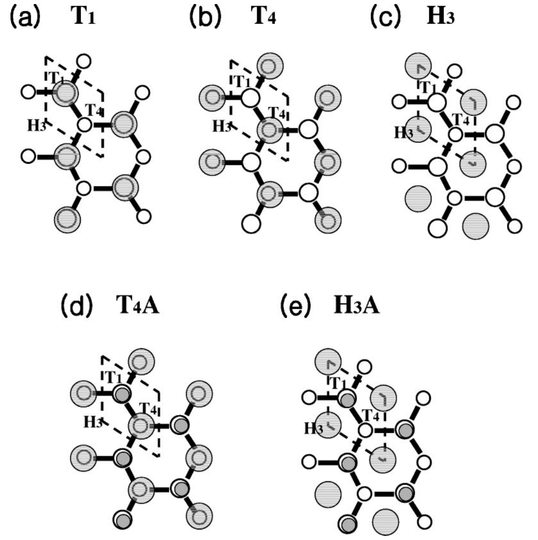

FIG. 2. Top view of five structural models for the Tl-induced Si(111)-1×1 surface. Each model is named by the designated binding site of a Tl atom. Large (small) filled circles represent Tl (Si) atoms and large (small) open circles denote Si atoms in the first (second) layer Si_1 (Si_2). Three high-symmetry binding sites T_1, T_4, and H_3 are marked in each unit cell drawn by the dashed parallelograms. Another Si adatom is added on top of the Si_1 atom at the T_1 site for T_4A and H_3A models.

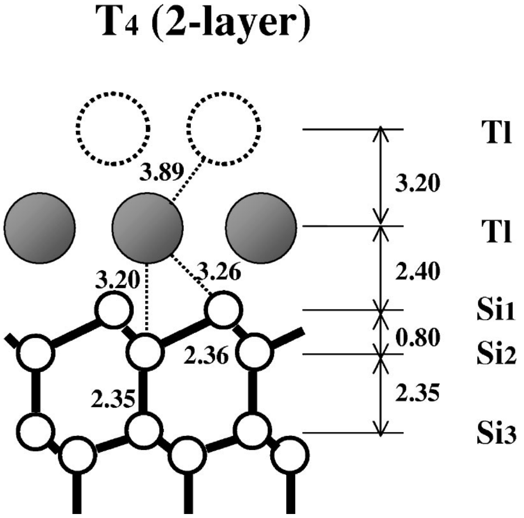

FIG. 3. Side view of the T_4 model with partially occupied Tl atoms in the second Tl overlayer. Large filled (dotted) circles represent Tl atoms in the first (second) Tl overlayer. Small open circles represent underlying Si atoms. The bond lengths obtained from the fits are shown near the bonds associated. A bond length for a bulk Si is 2.35 Å.

The two sets of CTR curves obtained from the Tl-induced Si(111)-1×1 surface are presented in Figs. 1(b)–1(d), where open (closed) circles with error bars are data points measured for CTRs at A (B). These CTR curves pass through the integer-order (0 0), (1 0), and (1 1) spots. We have tried to fit the CTR curves by adopting five structural models distinguished mainly by different Tl-Si bonding geometry. The structural models are schematically drawn in Fig. 2 and will be discussed in detail in the following paragraph. Although three types of fit curves are shown in Fig. 1 for the three structural models—T_1 (dashed), T_4 (solid), and H_3 (dotted)—one easily finds that the solid fit curves based on the T_4 model best describe our experimental data. As determined by the full width at half maximum of 0.022° of a ϕ scan for a reflection ($10L$) at $L=0.1$ r.l.u., the Tl-induced 1×1 surface turns out to be quite flat with a correlation length greater than 2700 Å. Furthermore, the surface remains almost unaltered during measurements, as seen by the small intensity variation, which is less than 5%. The significantly enhanced intensity between Bragg peaks compared to that of the CTR from the Si(111) surface indicates much enhanced scattering from the heavier Tl atoms. As demonstrated in Figs. 1(b)–1(d) by the distinctly different fit curves depending on the structural models, the intensity variation near the Bragg peaks most sensitively reflects the detailed atomic arrangement, including relaxation. Such a feature is most significant for the CTR of ($10L$) in Fig. 1(c).

We now describe the in-plane arrangements of the five structural models sketched in Fig. 2 (refer to Fig. 3 for the out-of-plane arrangements). The models are distinguished essentially by Tl atoms occupied at different high-symmetry binding sites. Since the simplest structural model for the 1×1 surface contains one atom per unit cell, we first consider the three high-symmetry lattice sites—T_1, T_4, and H_3—as plausible binding sites for a Tl adatom to occupy with only one Tl atom per unit cell. From the fact that a bulk-truncated Si(111) surface has only one dangling bond from a Si_1 atom at the T_1 site (see Fig. 3), a T_1 model in Fig. 2(a) where Tl atoms occupy the T_1 sites is favored if Tl behaves as a monovalent atom.[5] Recent calculation[8] and LEED $I(V)$ study,[9] however, prefers a T_4 model to the T_1 model. In the T_4 model [Fig. 2(b)], Tl atoms occupy the T_4 sites by bonding with three neighboring Si_1 atoms to show their trivalent nature. Although an H_3 model in Fig. 2(c) is then equally plausible with the T_4 model, it is energetically less favorable as shown in previous calculation.[8] Another possible model T_4A in Fig. 2(d) [or an H_3A in Fig. 2(e)] has one more Si adatom added to the Si_1 atom at the T_1 site, so that Tl atoms may couple with these three additional Si adatoms. We have, however, excluded a passivated arsenic-terminated surface model,[16] where metal atoms take the place of the outermost Si atoms at the T_1 sites, since this model is equivalent to our H_3A model.

These models have been examined by fitting the experimental CTR curves with the calculated structure factor F_{HKL} given below

$$F_{HKL}=\sum_j \theta_j f_j \exp(-B_j\mathbf{Q}^2/16\pi^2) \times\exp(-2\pi i(Hx_j+Ky_j+Lz_j)),$$

where the sum is over all the atoms with atomic scattering factor f_j in the unit cell. We have varied only the out-of-plane displacements of atoms including Tl in order to preserve the 1×1 in-plane symmetry. Two other parameters such as the layer occupancy θ_j and the Debye parameter B_j

for Tl have been used as the additional fit parameters. The Debye parameter is related to the mean-squared displacement amplitude $\langle u_j^2 \rangle$ by $B_j = 8\pi^2 \langle u_j^2 \rangle$. The Debye parameter for Si atoms was fixed with a bulk value of 0.45 Å^2.[3] As for previous study,[17] the surface roughness σ was set to zero since any fit we have performed including σ as a fitting parameter results in a negligibly small value of σ. The final best-fit structure was determined through a least-squares minimization of the reduced χ^2 value, and was also cross-checked by the unweighted residuum R factor.[18]

In the fitting, we first varied only Tl atoms with all the Si atoms frozen at their bulk positions. At this stage, the T_4 model is unequivocally favored over other models by the least χ^2, which is in good agreement with previous reports.[8,9] We find the same result even when Si$_1$ atoms in addition to Tl atoms are varied despite the slightly reduced values for other models. More specifically, we obtain $\chi^2=23.1$ (26.4) and 14.5 (18.6) for the T_1 and H_3 model, respectively, with the CTRs at B (A), which are significantly greater than $\chi^2=1.9$ (3.2) of the T_4 model. The fitted CTR curves are presented as dashed, solid, and dotted curves for the T_1, T_4, and H_3 models in Fig. 1. As concluded earlier, the T_4 model is clearly favored over other models. We have also ruled out the T_4A (H_3A) model (not shown in Fig. 1) simply because of its greater χ^2, with the resulting bonding geometry being much different from the expected position. We thus conclude with confidence that the T_4 model best describes the atomic structure of the Tl-induced 1×1 surface.

Although varying more Si atoms including Si$_2$ atoms in the second layer with the T_4 model improves χ^2 slightly, the resulting atomic structure shows unusually large expansion of the Si$_2$-Si$_3$ interatomic distance. Such a large expansion (or contraction) is thought to be unreasonable when considering the rigidity of the Si-Si bonding in a covalently bonded structure. As an additional check to determine whether any error is involved in our fittings, we repeated them with frozen Si atoms down to the third layer. We found that the interatomic spacings in the deeper layers (⩾ third layer) do not converge quickly to the bulk values. Instead they become unphysically large. We found the same tendency when we varied all the Si atoms. We, therefore, have fixed Si atoms in the deeper layers beyond the second layer into the bulk structure.[3]

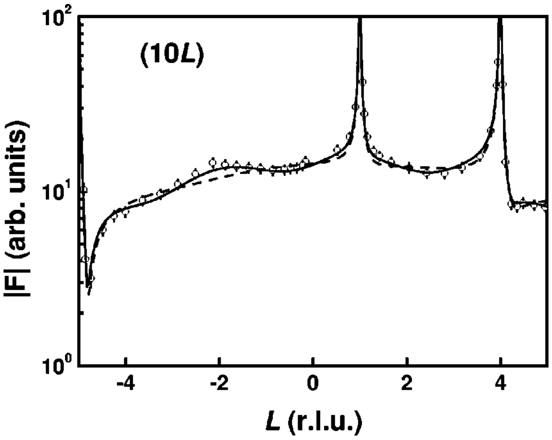

FIG. 4. Fitting our experimental structure factors (open circles) along the (10L) CTR at B based on a T_4 model with only one Tl overlayer (dashed curve) and with two Tl overlayers (solid curve). The two Tl overlayer model apparently improves fitting especially in the region between Bragg peaks.

When Tl atoms directly above top-layer Si atoms in the second Tl overlayer (see Fig. 3) are varied additionally, χ^2 improves further by about 34%, i.e., from 3.2 to 2.1 for the CTRs at A (or by about 26% from 1.9 to 1.4 for those at B). This two-Tl-layer model fits our experimental CTR data

TABLE I. Results for the fit parameters from the refined T_4 model under the restriction of one layer or two layers of Tl atoms. Si$_1$ atoms and Tl atoms were varied with any other Si atoms fixed at their bulk values in fitting the experimental CTR curves. Resulting interatomic distances are also compared to those reported earlier by a density-functional theory (DFT) calculation and by a LEED $I(V)$ analysis. Si$_1$ (Si$_2$, Si$_3$): Si atoms in the first (second, third) layer.

	CTR set A		CTR set B			
Fit parameters	T_4 with one layer	T_4 with two layers	T_4 with one layer	T_4 with two layers	DFT (Ref. 8)	LEED (Ref. 9)
χ^2	3.2	2.1	1.9	1.4		
R factor (%)	9.4	7.5	7.4	6.2		
Debye parameter for Tl (B)	4.8±0.1	4.0±0.1	3.8±0.1	3.8±0.1		
Occupancy of the 1st-layer Tl	0.264±0.002	0.267±0.002	0.70±0.01	0.73±0.01		
Occupancy of the 2nd-layer Tl		0.035±0.002		0.06±0.01		
Interatomic distance (Å)						
Tl-Tl		3.94±0.03		3.89±0.04		
Tl-Si$_1$	3.26±0.01	3.25±0.01	3.32±0.02	3.26±0.02	3.13	3.17
Tl-Si$_2$	3.17±0.01	3.18±0.01	3.21±0.01	3.20±0.01	3.08	3.16
Si$_1$-Si$_2$	2.35±0.01	2.36±0.01	2.34±0.01	2.36±0.01	2.38	2.39
Si$_2$-Si$_3$	2.35[a]	2.35[a]	2.35[a]	2.35[a]	2.34	2.28

[a] Bulk value.

much better than the one-Tl-layer model, as shown in Fig. 4. We are thus led to conclude that the atomic arrangement with two Tl layers shown in Fig. 3 best represents the atomic structure of the Tl-induced 1×1 surface. The results from the fits are listed in Table I. The Debye parameter, $B=3.8\pm0.1$, obtained is comparable to a typical value for other heavy metal atoms adsorbed on the Si surface. The number of Tl atoms in the top second layer reaches about 10% of that in the first layer. The occupancy parameters indicate that the Tl coverage estimated is ~0.3 and ~0.8 for the CTRs at A and B, respectively. These values are underestimated compared to those assigned as 0.5 ML and 1.0 ML shown in Fig. 1(a). Interestingly, the two Tl layers are found to be relaxed compared to a Tl bulk, as seen by the increased interlayer spacing of 3.20 Å, which is greater than the bulk value of 2.76 Å.[19] The interatomic spacing between Si_1 and Si_2 atoms appears to be increased slightly as predicted by the density-functional-theory (DFT) calculation.[8] The Tl-Si bond lengths are found also to be slightly greater than those calculated or determined by LEED analysis. The overall atomic structure determined in this work based on the T_4 model, however, is in excellent agreement with that from previous studies. An important conclusion one may draw from our result is that the bonding nature of Tl-Si is ionic rather than covalent in order to saturate the dangling bonds of Si_1 atoms. Earlier DFT calculation suggests that Tl donates a portion of its charge to adjacent Si atoms to make the Tl-Si partially ionic.[8]

In summary, we report the atomic structure of the Tl-induced 1×1 phase formed on the Si(111) surface by analyzing our experimental CTR curves obtained by using synchrotron x-ray scattering. We find that the two-Tl-layer model with Tl atoms that occupied the T_4 binding sites best describes the Tl-induced 1×1 surface. Our results provide the most accurate atomic structure not hindered by multiple scattering effects in LEED, and they confirm the T_4 binding sites as the most stable binding sites for Tl, as suggested earlier.[8,9]

This work was supported in part by X-ray/particle-beam Nanocharacterization Program (RN0326). D.Y.N. acknowledges support from the Korean Science and Engineering Foundation under Grant No. R01-2002-000-00469-0.

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[18] $\chi^2=1/(N-P)\Sigma\{[(|F^c_{HKL}|-|F^o_{HKL}|)^2]/\sigma_F^2\}$; here, N is the number of data points and P is the number of free parameters. The superscript "o" refers to the observed values and "c" to the calculated values. The corresponding R factor is defined as $R=(\Sigma||F^c_{HKL}|-|F^o_{HKL}||)/\Sigma|F^o_{HKL}|$.

[19] The bulk Tl has a hcp structure with lattice constants of $a=3.46$ Å and $c=5.52$ Å.