

Long-period modulations in the linear chains of Tl atoms on Si(100)A. A. Saranin,^{1,2,3} A. V. Zotov,^{1,2,4} I. A. Kuyanov,² V. G. Kotlyar,² M. Kishida,¹ Y. Murata,² H. Okado,⁵ I. Matsuda,⁶ H. Morikawa,⁶ N. Miyata,⁶ S. Hasegawa,⁶ M. Katayama,¹ and K. Oura¹¹*Department of Electronic Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan*²*Institute of Automation and Control Processes, 690041 Vladivostok, Russia*³*Faculty of Physics and Engineering, Far Eastern State University, 690000 Vladivostok, Russia*⁴*Department of Electronics, Vladivostok State University of Economics and Service, 690600 Vladivostok, Russia*⁵*Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Ibaraki, Osaka 567-0047, Japan*⁶*Department of Physics, School of Science, University of Tokyo, Tokyo, Japan*

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The room-temperature 2×1 structure at the one-monolayer Tl/Si(100) 2×1 surface has been found to undergo a temperature-induced reversible transition into the ground-state $(6,1) \times (0,6)$ structure through the formation of the intermediate “ $c(4 \times 7)$ ” structure. The transition is interpreted as an order-disorder transition due to hopping fluctuation of Tl atoms in the chains. The transition is associated with developing of the long-periodic transverse wandering in the chains of Tl atoms through an interchain interaction.

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Semiconductor surfaces with and without adsorbates have been proved to be the most suitable playground to study phase transitions in low-dimensional systems. Various transition scenarios have been observed in these studies.^{1,2} For $2 \times 1 \leftrightarrow c(4 \times 2)$ transition at the clean Si(100)³ and Ge(100)⁴ surfaces, as well as for the $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ at Pb/Ge(111)⁵ or Sn/Ge(111)⁶ surfaces, the atom fluctuations are up and down⁷ accompanied by charge redistribution. For usual charge-density-wave (CDW) transition like $4 \times 1 \leftrightarrow “8 \times 2”$ at In/Si(111) surface,⁸ the atom shifts are longitudinal along the chain (e.g., pairing along the chains). At the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag surface,^{9–11} the atoms shift rotationally around the center of Ag triangles. What we learn from these examples is that the atoms at surfaces dynamically fluctuating at room temperature, which is not a random thermal vibration. The fluctuations are correlated to each other with the neighboring atoms, due to a short-range order in the ground-state structure at low temperatures. The phase transitions at surfaces are thus always related to some kinds of fluctuation and modulations in atomic positions.

In the present study of the phase transitions taking place at Si(100) 2×1 -Tl surface at reduced temperatures, we have found a new type of behavior, namely, formation of the long-wavelength modulations which are caused by transverse hopping of Tl atoms in the chain structure among three stable positions. Through the interchain interaction, the modulations lead to a formation of two-dimensional superstructures.

Scanning tunneling microscopy (STM) observations were performed with Omicron variable-temperature STM operated in an ultrahigh vacuum ($\sim 1 \times 10^{-10}$ Torr). Atomically-clean Si(100) 2×1 surfaces were prepared *in situ* by flashing to 1250 °C after the samples were first outgassed at 600 °C for several hours. Thallium was deposited from a Ta foil tube or from an alumina basket at a rate of about 0.15 ML (monolayer)/min. The angle-resolved photoemission spectroscopy (ARPES) measurements were carried out on the samples held at room temperature (RT) with photon energies of He I (21.2 eV) and He II (40.8 eV) radiation and with Gammadata Scienta analyzer SES-100.

As has recently been shown,¹² the 1-ML Tl/Si(100) 2×1 phase is formed upon saturating adsorption of Tl onto Si(100) 2×1 surface held at temperatures from RT to about 270 °C [at higher temperatures Tl does not stick to the Si(100) 2×1 surface]. According to the total-energy calculations,¹² the Tl/Si(100) 2×1 phase is built of Tl adatoms occupying the pedestal and valley-bridge sites on the Si(100) surface which preserves its original dimer-row structure (Fig. 1). Note that the atomic arrangement of the Tl/Si(100) 2×1 phase is akin to the structure which is commonly accepted for the 2×1 reconstructions induced by alkali metals at 1 ML coverage (the so-called double-layer model proposed by Abukawa and Kono¹³).

At room temperature in the defect-free regions, the Tl/Si(100) 2×1 phase shows up in the filled-state STM images as straight rows of oval-shaped protrusions [Fig. 2(a)]. These rows have been established¹² to be located along the Si-dimer rows and the oval protrusions are plausibly located in the pedestal sites. In the RT empty-state STM images (at absolute bias voltages above ~ 1 V), one sees the blurred

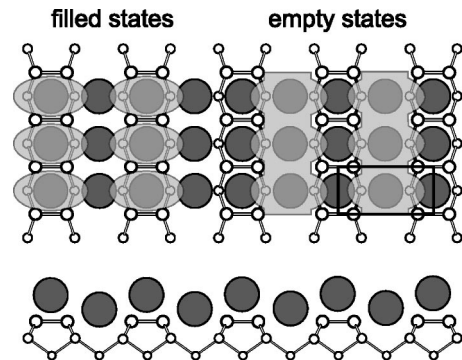


FIG. 1. Top and backside view of the 1-ML Tl/Si(100) 2×1 structural model. Location of the filled-state (left panel) and empty-state (right panel) STM protrusions is indicated. Tl atoms are shown by dark gray circles, Si atoms by white circles. 2×1 unit cell is outlined.

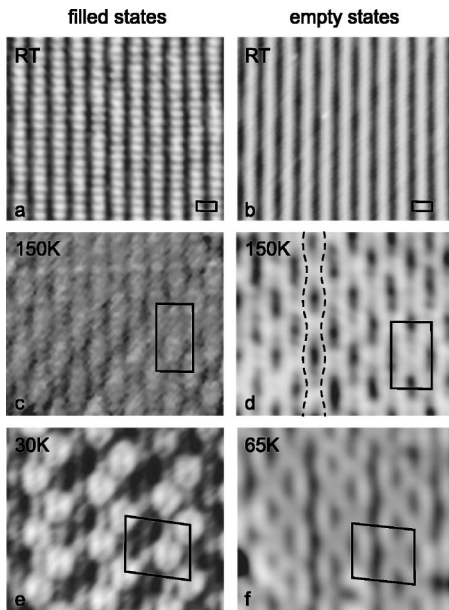


FIG. 2. Filled-state (left column) and empty-state (right column) STM images ($85 \times 75 \text{ \AA}^2$) showing the structural evolution of the TI monolayer on Si(100) upon cooling the sample. The sample temperature is RT for (a) and (b), 150 K for (c) and (d), 30 K for (e), 65 K for (f). The unit cells are outlined. The dashed lines along two neighboring rows in (d) are to illustrate that they show up as two antiphase transverse waves.

rows [Fig. 2(b)]. They have been found¹² to locate along the troughs between the Si-dimer rows. Thus, one can conclude that the rows seen in the filled states are associated with the upper rows of TI atoms residing in the pedestal sites above the Si-dimer rows, while rows seen in the empty states are related to the lower rows of TI atoms occupying the valley-bridge sites in the troughs (see Fig. 1).

As the sample temperature is lowered (say, to 150 K), the STM appearance of the TI/Si(100) phase changes. In the filled states, the straight rows become width-modulated [see Fig. 2(c)], while rows in the empty states obtain a shape of the transverse waves [see Fig. 2(d)]. In both polarities, the row modulations in the neighboring rows are in the antiphase, thus a centered rectangular 2D lattice is formed. As illustrated in Fig. 3, the segment of the row which displays in the filled states the maximal width and brightness correspond to the place where two neighboring antiphase waves in the empty states have the closest proximity (“meet” each other).

It should be noted that the modulated-row structure develops already at RT in the vicinity of surface defects such as missing-dimer defects, C defects and step edges (see Fig. 4). The modulation waves generated by the neighboring defects interfere with each other, that often leads to the local variations of wave period. An averaged value determined at RT using FFT analysis appears to be about $7a_0$, as seen also in Fig. 3(b) hence the structure can be notated as “ $c(4 \times 7)$.” Presence of the defects hampers accurate determination not only of the precise periodicity of this structure but also of the exact temperature of the 2×1 -to-“ $c(4 \times 7)$ ” transition.

When the temperature is lowered to about 120 K, the surface structure changes to that shown in Figs. 2(e) and 2(f).

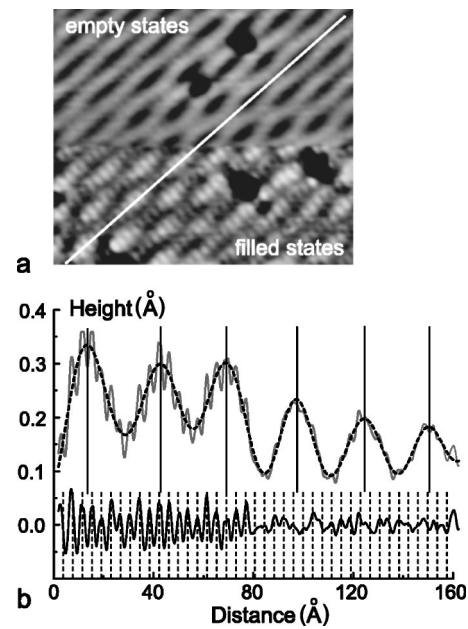


FIG. 3. (a) Dual-polarity STM image of the Si(100)-“ $c(4 \times 7)$ ” structure. The lower part of the image was acquired with negative sample bias, the upper part with positive sample bias. (b) The profile (solid curve) along the line shown in (a). The envelope line of the line profile is shown by dashed curve. The curve in the low panel represents the line profile after subtracting the envelope. The period of the dashed grid is $a_0 = 3.84 \text{ \AA}$, the period of the solid grid is about $7a_0$.

This structure preserves down to 6 K, the lowest temperature used in this study. The most apparent feature of the new structure is the developing of the $6a_0$ periodicity in the direction perpendicular to the rows. In the filled states, this periodicity is manifested as a consequence of two modulated rows followed by one straight narrow row. In the empty states, the central row in the group of three wavy rows has a larger transverse amplitude, while the two edge rows have a smaller amplitude. The latter results in developing the dark wavy “gaps” which separate the three-row groups from each other. More close examination of the structure reveals that

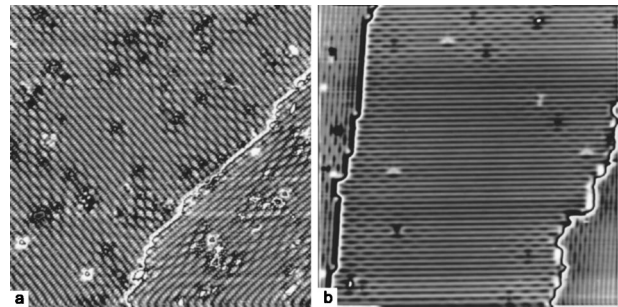


FIG. 4. (a) Filled-state and (b) empty-state STM images of the TI/Si(100) surface at RT. The “ $c(4 \times 7)$ ” structure develops near the surface defects, while defect-free regions preserves the 2×1 structure. Scale of the images is $430 \times 430 \text{ \AA}^2$. To improve visualization of the reconstruction on the neighboring terraces, (a) two and (b) three gray scales were used. Thus, the lines in the images correspond to the atomic step edges.

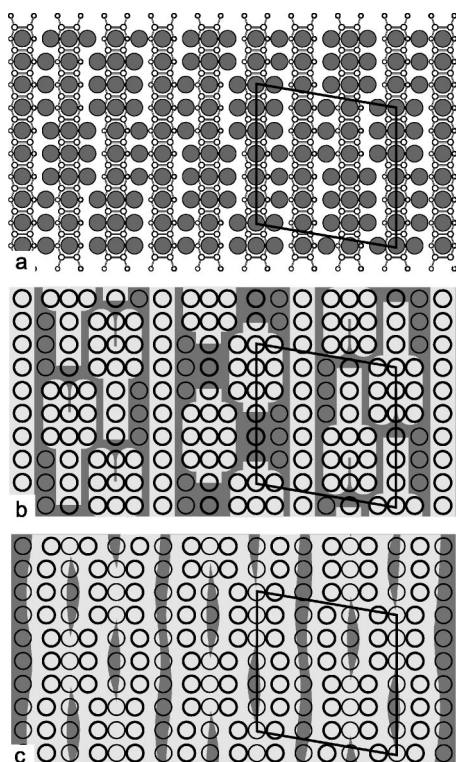


FIG. 5. (a) Structural model of the low-temperature 1-ML Si(100)(6,1) \times (0,6) phase. Schematic sketches of the (b) filled-state and (c) empty-state STM images superposed with the location of the TI atoms adopted by the model. STM maxima and depressions are shown bright and dark, respectively.

the modulation period along the rows becomes $6a_0$ and the features in the adjacent three-row groups are shifted along the row direction by a_0 , i.e., the periodicity of the structure is expressed in matrix notation as $\begin{pmatrix} 6 & 1 \\ 0 & 6 \end{pmatrix}$ or as (6,1) \times (0,6). Formation of the symmetric (6,-1) \times (0,6) domains also takes place.

Taking into account the bias-dependent STM appearance of the 1-ML Ti/Si(100) overlayer (Figs. 2 and 3) and its plausible structural model (Fig. 1), it is natural to assume that the long-range reconstructions developed upon cooling are mainly due to the displacements of Ti atoms in the linear chains occupying the troughs between Si dimer rows, namely, correlated shifts of Ti atoms from basic valley-bridge position convert the straight chain into that having a shape of the transverse wave. Thus, the ground-state (6,1) \times (0,6) structure can be represented by the model shown in Fig. 5(a). In the model, the Ti rows lying in the troughs between the Si-dimer rows are built of three-atom segments in which all three atoms occupy the same sites, i.e., centered or off-centered valley-bridge sites. The off-centered segments in the neighboring rows are linked to each through three Ti atoms in the pedestal sites, thus forming the groups of three parallel Ti trimers. The $6a_0$ periodicity in the direction perpendicular to the rows is due to the fact that every third row contains Ti atoms only in the off-centered sites while in the other two rows Ti atoms reside both in the off-centered and centered valley-bridge sites. Correspondence of this atomic configuration to the observed STM images is illustrated in Figs. 5(b) and 5(c).

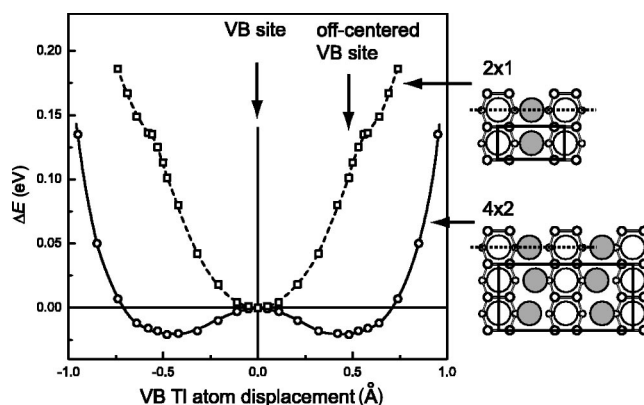


FIG. 6. Variation of the energy per 2×1 unit cell versus displacement of valley-bridge (VB) atom (shaded in the sketches of the model structures) along the axis shown by dotted line in the model structures. Squares and dotted curve show the results of the model calculations for the 2×1 unit cell, circles and solid curve are those for the 4×2 unit cell. In the ground-state 4×2 model structure, Ti atoms in the troughs occupy the off-centered VB sites forming antiphase zigzag chains.

To check the validity of the proposed structure, we have conducted first-principles total-energy calculations which details are given elsewhere.¹² Unfortunately, our computational abilities were not sufficient to conduct calculations for the real (6,1) \times (0,6) structure having large unit cell and we have carried out the calculations for much smaller unit cell, e.g., for the 4×2 one. These model calculations demonstrate that interaction between Ti atoms within the row can result in developing the additional wells in the off-centered valley-bridge positions (Fig. 6). The off-centered sites have been found to be located ~ 0.48 Å away from the centered valley-bridge site. The barrier separating the wells is of about 20–25 meV. The calculations for the 4×2 unit cell show that in the ground state Ti atoms occupy off-centered sites forming zigzag chains which are in antiphase with each other between the neighboring chains, as shown in the sketch of the model structure in Fig. 6. Thus, the simplified model calculations reproduce qualitatively some general features of the proposed low-temperature Ti/Si(100) structure.¹⁴

In the framework of this approach, the observed phase transitions can be understood as follows. As the barriers between the wells within the troughs are low, at temperatures of around RT the Ti atoms are free to hop between the wells. The hopping of Ti atoms is noncorrelated and no long-range ordering develops. As a result, an averaged picture seen in STM at RT [Figs. 2(a) and 2(b)] displays a 2×1 structure with straight rows of uniform width. Only in the vicinity of the surface defects, where Ti atoms are bound to one of the wells more tightly, local regions with the ordered modulated structure is observed [the behavior similar to that known for the buckled Si dimers on the pristine Si(100) surface]. At low temperatures of below ~ 120 K, the hopping is suppressed and all Ti atoms become trapped in their individual wells forming a ground-state configuration. As the 1-ML Ti/Si(100) interface shows up as a system of coupled chains, the transition to its ground-state structure occurs in two steps, i.e., represents the case described by a complex order

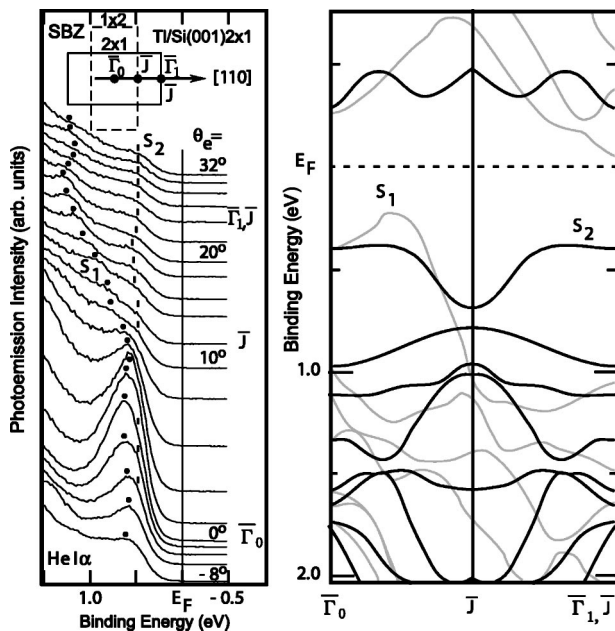


FIG. 7. (a) A set of ARPES spectra of the double-domain Si(001) 2×1 -Tl surface taken along the [110] direction with He $I\alpha$ radiation. The step in emission angles (θ_e) is 2 degrees between the neighboring spectra. The peak positions of different surface states assigned are marked with different symbols. Surface Brillouin zone (SBZ) of 2×1 (1×2) is indicated with symmetry points in the figure. (b) The band structure as determined from the first-principles total-energy calculations. The black and gray curves correspond to dispersions along $\times 2$ and $\times 1$ periodicities, respectively.

parameter.¹⁵ At the first step, a long-range ordering along the chains is adopted, as well as a short-range ordering between the neighboring chains. As a result, the “ $c(4 \times 7)$ ” structure is formed. At the final step, the long-range ordering between the chains develops and the ground-state $(6, 1) \times (0, 6)$ struc-

ture is formed. Note that developing of the long-range inter-chain ordering is accompanied by the change of the periodicity along the chains.

Consider the possible origin of the low-temperature ground-state reconstruction. One possibility is that the reconstruction is the result of local molecular-orbital-type bonding between Tl and Si atoms. Another possibility is that the reconstruction is due to periodic lattice distortions induced by CDW formation. Recall that for realization of the CDW mechanism it is required that the surface should be, at least, metallic at temperatures above the transition. However, the results of both ARPES measurements and total-energy calculations (see Fig. 7) indicate that the Si(100) 2×1 -Tl surface is semiconducting, ARPES does not reveal the presence of the filled states near the Fermi level; in the calculated band structure no surface bands cross the Fermi level. These results provide an argument against the CDW mechanism of the phase transitions. Thus, the ground-state reconstruction is believed to be controlled mainly by the interatomic interactions. In this case, the possible reason for the transverse wandering of the Tl atom chains is an aspiration to accommodate mismatch of atomic size of Tl and Si lattice constant. It should be noted, however, that due to the complexity of the long-period reconstruction other possibilities cannot be ruled out and actual mechanism driving the transition remains an open question and demands further elaborate consideration.

In conclusion, we have demonstrated that upon cooling the 1-ML Tl/Si(100) 2×1 surface undergoes a reversible transition to the ground-state $(6, 1) \times (0, 6)$ structure through the formation of the intermediate “ $c(4 \times 7)$ ” structure. The transition is believed to be of the order-disorder type taking place in the system with coupled linear atomic chains. The ground-state reconstruction is concluded to be driven by the interatomic interactions rather than by the collective electronic effects.

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¹⁴One should bear in mind that the model calculations provide only a tentative qualitative picture of the phenomenon. Direct extrapolation of these results for the real system seems to be hazardous, especially for the quantitative characteristics. For example, the calculations yield the value for the energetic barrier separating the wells of 20–25 meV. The transition takes place at a close kT , 120 K (i.e., ~ 10 meV). However, taking into account the vibration frequency, $\sim 10^{14}$ s⁻¹, one would expect much lower transition temperature.

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