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Interchain coupling of degenerated quasi-one-dimensional indium chains on Si(111)

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Interchain coupling of quasi-one-dimensional indium chains on the In/Si(111)-8×"2" surface has been investigated by low-temperature scanning tunneling microscopy. We find that the longitudinal periodicity doubling is caused by pairing effects of inner indium atoms, as well as outer indium atoms, within the zigzag chains below $T_c \sim 130$ K. Whereas poor long-range order observed in the transverse direction is attributed to the nearly degenerate chains, macroscopic interchain coupling is suggested to stabilize the quasi-one-dimensional charge-density-wave phase.

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Self-assembled atomic chains formed on silicon substrates have attracted much interest, because of the quasi-one-dimensional electronic properties and its related phase transition.[1–3] A quasi-one-dimensional structure is known to be formed by adsorption of indium on a Si(111) surface, which exhibits a 4×1 structure at room temperature.[4–6] The In atoms of the room-temperature 4×1 phase form two parallel zigzag chains, in which each double chain is separated by an insulating silicon chain,[5] and a quasi-one-dimensional metallic character has been observed along the In chains.[4,6] Recently, the metallic 4×1 structure was reported to undergo a structural transformation accompanying a metal-insulator transition below $T_c \sim 130$ K,[7,8] which has been interpreted as a quasi-one-dimensional charge-density-wave (CDW) formation driven by a Peierls instability along the chains. The low-temperature phase has been characterized as the eighth-order spots and the half-order streaks in the transverse and longitudinal directions, respectively, by the high-energy electron diffraction, called an $8\times$"2" phase.[7]

In contrast to the simple CDW picture, Kumpf *et al.* argued, based on the surface x-ray diffraction (SXRD) results, that the phase transition should be attributed to a modification of the zigzag In chains into a formation of trimers, rather than the CDW transition.[9] As shown in Fig. 1(a), this model includes the indium trimers, principally characterized by pairing of outer indium atoms of the double zigzag chains. The half-order streaks were interpreted as a result of 4×2-subcell disorder associated with the intrinsic glide symmetry, although strong transverse coupling was indicated by the eighth-order spots. The obtained large displacement from the 4×1 structure disagreed with a simple quasi-one-dimensional CDW-driven transition, but other recent experiments revealed the atomic displacement to be negligible.[10,11] From the first-principle calculations with density functional theory, Cho *et al.* have also suggested that the phase transition is a structural change, because the 4×2 or 8×2 structure is energetically favored more than the 4×1 phase.[12] However, the calculated atomic position of the $8\times2(4\times2)$ structure is inconsistent with the SXRD results. Consequently, the ground state configuration of the low-temperature $8\times$"2" phase and its origin are still controversial, even though the room-temperature 4×1 phase has been well understood.[4–6]

These conflict results may arise from the complicated interchain coupling in the low-temperature $8\times$"2" phase, in which the poor interchain correlation was indicated by the

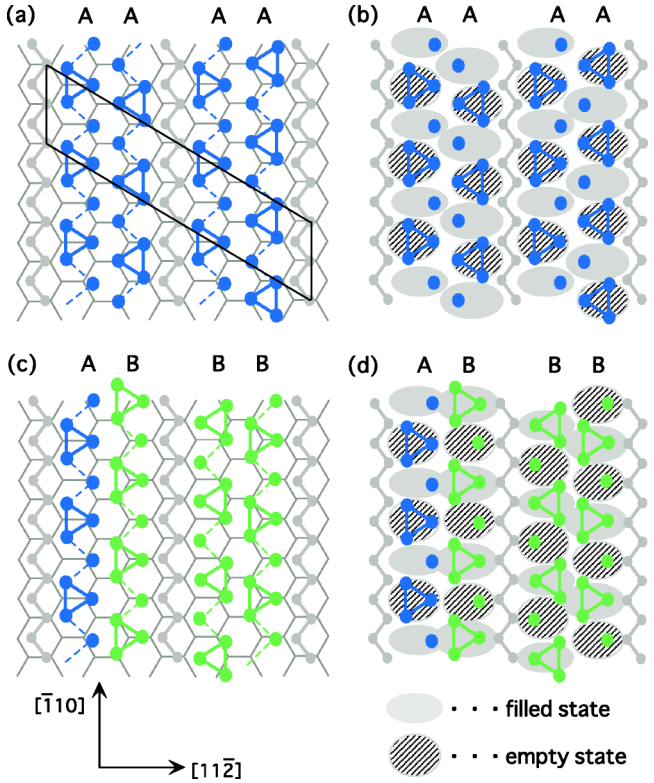

FIG. 1. (Color online) (a) Structural model of the In/Si(111)-8×2 surface reported by Kumpf *et al.* (Ref. 9). Blue (dark gray) dotted lines represent the zigzag indium chains of the 4×1 structure. In the 8×2 structure, the triangles are formed by a pairing effect of outer indium atoms in the zigzag chains. The 8×2 unit cell is indicated by a black solid line. (b) Expected STM protrusions in filled and empty states for the structural model of (a). (c) Additional structural model of the In/Si(111)-$8\times$"2" surface. As indicated by *B* [shown as green (light gray)], a pairing pattern of inner indium atoms is introduced, as well as that of outer indium atoms indicated by *A* [shown as blue (dark gray)]. In this model, the indium double rows consist of (*AB*) and (*BB*) configurations. (d) Expected STM protrusions in filled and empty states for the structural model of (c).

half-order streaks in the diffraction experiments even though the eighth-order spots lead to the long-range interchain ordering. Although the periodicity doubling along the In chains has been directly observed by scanning tunneling microscopy (STM), the detailed interchain coupling is still ambiguous. Furthermore, in general quasi-one-dimensional systems, the interchain interactions have a crucial role in the phase transition, because a strictly one-dimensional (1D) system with short range interactions does not develop long range order at finite temperatures.[13–15] Thus, the direct investigation of the interchain coupling in the In/Si(111) system should provide not only important insight into the formation mechanism of the $8\times$ "2" phase, but also an unique opportunity to understand how interchain interactions influence the long-range ordering in the quasi-one-dimensional system.

In this paper, we use low-temperature STM to visualize the interchain correlation of the quasi-one-dimensional indium chains on the In/Si(111)-$8\times$ "2" surface. By comparing the STM images and the structural model, we find that the periodicity doubling along the chains is caused by pairing effects of inner indium atoms, as well as outer atoms, within each zigzag chain, and both the structures are randomly distributed on the surface even at 6 K, leading to the half-order streaks in the reciprocal space. Whereas the ground-state configuration should be almost degenerate, the transverse eighthfold periodicity is observed to be associated with a faint contrast modulation in the direction perpendicular to the chains, which may be due to the out-of-plane periodic lattice distortion. We further discuss the details of the complicated interchain coupling of the In/Si(111)-$8\times$ "2" surface.

All experiments were carried out in an UHV chamber with a low-temperature STM, a base pressure of which was less than 1×10^{-9} Pa. The boron-doped Si(111) sample with a resistivity of $<0.1\ \Omega$ cm was cleaned by flashing up to 1420 K, and slowly cooled to room temperature. About two monolayers of In were then deposited onto the Si(111) clean surface at room temperature, followed by a brief anneal at around 630 K. The sample was subsequently transferred to the cooled STM stage. All STM images were acquired in a constant-current mode of 100 pA in a temperature range of 6–128 K.

Figure 2 shows filled- and empty-state STM images of the In/Si(111) surface at 63 K, where the In chains are formed in the $[\bar{1}10]$ direction. In contrast to the room-temperature 4×1 phase,[16] it is clearly visible that an enhanced contrast modulation with the twofold periodicity appears along the chains, and the paired zigzag indium chains are well resolved into double rows of prominent protrusions. Within the double rows, two adjacent brighter protrusions are tilted up or down with respect to the $[11\bar{2}]$ direction. Since the spatial resolution becomes poorer with increasing bias voltage, the brighter protrusion pairs are changed into an oval appearance in the filled-state STM images at high bias, as marked in Fig. 2(a) (see also Fig. 4). Such an oval appearance has been reported previously,[7,17,18] and the up-down sequence of the tilting directions has been considered to make the eighthfold transverse periodicity,[19] leading to the formation of the $8\times$ "2" phase. In the empty-state image, the periodicity doubling is also shown in Fig. 2(b), but the double rows are more clearly separated by intrachain trenches. The trenches become wider with increasing bias voltage (not shown), similar to the room temperature 4×1 phase.[16] Whereas the periodicity doubling appears along the chains both in the filled- and empty-state images, these images show complementary structures in the chain direction. As shown in Fig. 2(b), the topographic minimum in the empty-state image corresponds to the maximum in the filled-state image of Fig. 2(a). Thus the enhanced brightness with the twofold periodicity of the STM images should be attributed to the spatial redistribution of surface charge density with a small energy gap through the phase transition. This result supports the quasi-one-dimensional CDW picture.

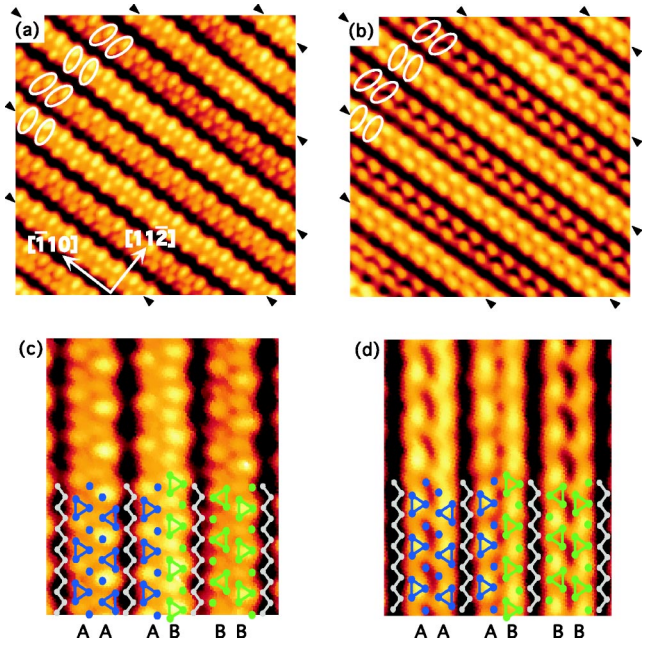

FIG. 2. (Color online) (a) and (b) Filled- and empty-state STM images (10.0×10.0 nm^2) of In/Si(111)-$8\times$ "2" surface at 63 K, obtained at a sample bias voltage V_s of -0.4 and $+0.4$ V, respectively. Tilted ovals in (a) and (b) represent the positions of the topographic maximum in the filled-state image. Black arrows denote the brighter rows. (c) and (d) Enlarged filled- and empty-state STM images (5.1×4.3 nm^2) of In/Si(111)-$8\times$ "2" surface at 63 K, obtained at $V_s=-0.4$ and $+0.5$ V, respectively. The structural model is superimposed on.

In order to clarify the structural configuration of the low-temperature $8\times$ "2" phase, we have compared the high-resolution STM images with the structural model obtained by the SXRD experiment.[9] In contrast to the $8\times$ "2" phase, the room-temperature 4×1 phase has been well understood by theory and experiment.[4–6,16] For the bias-dependent STM images of the 4×1 phase it has been reported that inner In atoms of the two zigzag chains are mainly probed in the filled-state and the *low-bias* empty-state images, and outer In atoms are probed in the *high-bias* empty-state images ($V_s>+1.0$ V).[16] In the 8×2 structural model of Fig. 1(a), the indium trimers are principally formed by a pairing effect of outer indium atoms, and thus the paired outer atoms are expected to be probed in the high-bias empty-state image.

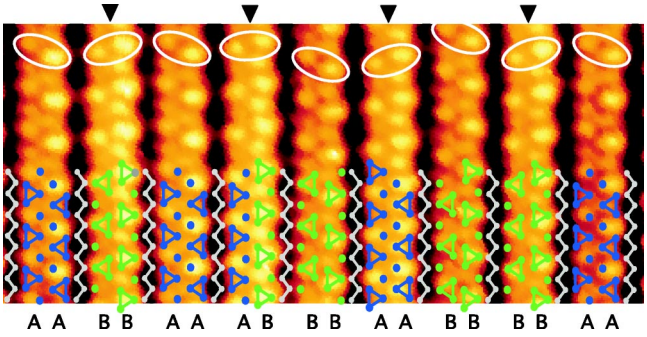

FIG. 3. (Color online) Filled-state STM image (5.1×12.0 nm^2, $V_s = -0.4$ V) of In/Si(111)-8×"2" surface at 63 K with the structural model.

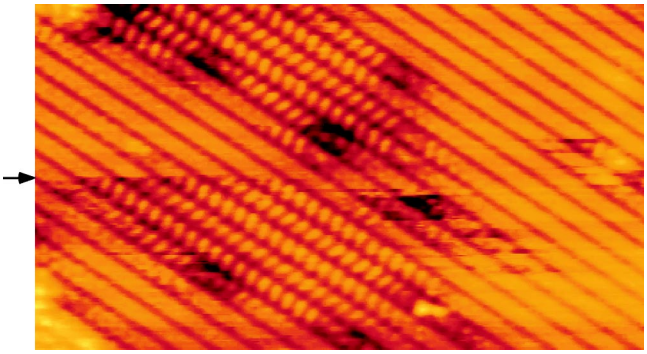

FIG. 4. (Color online) Filled-state STM image (20.0×35.0 nm^2, $V_s = -0.3$ V) of In/Si(111) surface at 128 K. At the line pointed by an arrow, the 8×"2" domain is suddenly nucleated during the STM scan, in which the up-down sequence of the tilted oval protrusions leads to the "appearing" eighthfold periodicity.

Between higher- and lower-bias empty-state images, we did not observe topographic shifts in the chain direction of the 8×"2" phase. Consequently, the brighter protrusions in the lower- and higher-bias empty-state images can be assigned to the inner and the outer indium atoms of the trimers, respectively, whereas the isolated indium atoms should be probed in the filled-state images. The expected protrusions obtained in the filled- and empty-state STM images are illustrated in Fig. 1(b). However, our detailed analysis based on the above assumption reveals that the high-resolution STM images are not fully consistent with the structural model of Fig. 1(a). When the model structure is superimposed on the STM images, the phase of the periodicity doubled chains is frequently shifted from the expected positions by half a primitive unit cell, i.e., $\times 1/2$, in the chain direction. This $\times 1/2$ phase shift cannot be explained by the 4×2-subcell disorder associated with the glide symmetry.

To interpret the STM images, we introduce an additional model, in which inner indium atoms are displaced to form pairs, as shown in the right-side chains of Fig. 1(c). In this structure, the paired inner atoms are expected to be highlighted in the filled-state image, whereas the isolated outer indium atoms should be observed in the empty-state image, as illustrated in Fig. 1(d). The pairing models of outer and inner indium atoms are labeled as *A* and *B*, respectively. Assuming that these structures coexist on the surface, the indium double rows can be classified into (*AA*), (*AB*), (*BA*), or (*BB*) configurations as indicated in Fig. 1. Figure 2 shows a precise comparison of the STM images and the structural model with the (*AA*)(*AB*)(*BB*) sequence, which shows good agreement both in the filled and empty states. As shown in the larger STM images of Fig. 3, it is obvious that the four types of the configuration are randomly distributed on the surface at 63 K, whereas the probability of the (*AA*) and (*BB*) configurations is slightly higher (~68%). Even though macroscopic interchain interactions are indicated by the up-down sequence of the tilted protrusion pairs, this random arrangement leads to poor long-range order on an atomic-level precision in the direction perpendicular to the chains. This suggests the presence of a $N \times 2$ superstructure of varying periodicity *N* across the periodicity doubled chains, which causes the half-order streaks in the diffraction patterns. Furthermore, we have observed that the random arrangement still preserved even at 6 K, in accordance with the SXRD result that revealed the half-order streaks at 20 K.[9] From this, the ground-state configuration is expected to be almost degenerate.

Nevertheless, the well-developed eighth-order spots have been observed by several diffraction experiments,[7,9,11] which suggests the long-range interchain ordering. Although this result disagrees with the poor interchain correlation of the periodicity doubled rows discussed above, we find an additive contrast modulation in the direction perpendicular to the chains from the high-resolution STM images. As indicated by arrows in the filled- and empty-state images of Fig. 2, the brighter rows are alternately ordered into a striped shape, leading to the eighthfold transverse periodicity. The height difference was estimated to be only about 0.015 nm, which was observable at low-bias voltage, but almost independent of the bias polarity. Note that such a faint striped shape is difficult to distinguish from the usual resolution STM images as reported earlier.[7,17–19] Owing to the alternate ordering of the bright rows, the eighth-order spots are indeed obtained in the Fourier transform of the high-resolution STM images (not shown). The Fourier transform has also revealed the half-order streaks originated from the poor interchain correlation of the periodicity doubled rows, in agreement with the 8×"2" phase.

Perpendicular to the chains, the contrast modulation of the STM images may be attributed to the out-of-plane lattice distortion in the top and/or subsurface layers rather than the electronic rearrangement, due to the bias polarity independency. We have further observed that the out-of-plane lattice distortion is correlated with the up-down sequence of the tilted protrusions pairs. As shown in Figs. 2(a) and 3, it is apparent that all the brighter rows are composed of the "tilt-up" protrusion pairs. Thus, the transverse ordering of CDWs should be strongly coupled to the out-of-plane periodic lattice distortion, even though the four configurations of the rows are almost degenerate. Hence, we have confirmed such an interchain coupling by the STM investigation around $T_c \sim 130$ K. As shown in the filled-state image at 128 K of Fig. 4, the 8×"2" phase is formed locally and is fluctuating in this temperature range, whereas most of the indium chains

exhibit the 4×1 phase. At the middle point of Fig. 4, the $8\times$"2" domain has suddenly been nucleated during the STM scan. The local formation of the $8\times$"2" phase is apparently correlated with the interchain correlation; the nucleated domain is expanded in the direction perpendicular, as well as parallel, to the chains. In addition, the up-down sequence of the tilted ovals is accompanied with the structural nucleation. This result accords with the diffraction experiments that the eighth-order spots and the half-order streaks appear simultaneously during the phase transition. However, it should be emphasized again that the atomic-level long-range order is absent in the direction perpendicular to the chains as shown in Fig. 3.

A plausible explanation for the poor interchain correlation should be that the system is closed to the strictly 1D, so that the interaction energy is almost identical among the four types of configurations. Nevertheless, the long-range force by the electronic Coulomb interactions between CDWs should be exercised within and across the double rows, leading to the up-down sequence of the tilted protrusion pairs. This interchain correlation should result in stabilizing the quasi-one-dimensional CDW state below about 130 K as shown in Fig. 4. It should be noted that these phenomena cannot be explained by the simple structural phase transition.[9,12] Although the random arrangement of the chains is preserved even at 6 K, we conclude that the macroscopic interchain coupling, such as the up-down sequence of the tilted protrusion pairs and the alternate ordering of the bright rows, may develop nearly-long-range order in this system below about 130 K, which gives rise to the formation of the $8\times$"2" CDW phase. This explains the reason that the eighth-order spots have been observed simultaneously with the half-order streaks in the low-temperature phase.

In summary, the complicated interchain coupling of the quasi-one-dimensional indium chains has been investigated by low-temperature STM. From the high-resolution STM images, we found that the longitudinal periodicity doubling in the low-temperature $8\times$"2" phase is caused by the pairing effects of the inner indium atoms, as well as the outer atoms, within the zigzag chains. The almost identical interaction energy between the chains should lead to the absence of the transverse long-range order on an atomic level even at 6 K, giving rise to the half-order streaks in the reciprocal space. Nevertheless, the STM images revealed the well-ordered up-down sequence of the tilted protrusion pairs and the alternate ordering of the bright rows, which should be attributed to the macroscopic interchain coupling originated by the Coulomb interactions within and across the indium rows. As a result, the macroscopic interchain coupling would stabilize the quasi-one-dimensional CDW state below $T_c\sim130$ K even without the atomic-level transverse order. Although further theoretical analysis is required to understand the complicated interchain correlation in this system, the interchain coupling generally acts as an important role for quasi-one-dimensional systems. We believe that the real-space investigation of the interchain coupling presented here provides important insights into a deep understanding of the ordering phenomena in general quasi-one-dimensional systems.

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