Real-Space Observation of Nanoscale Inhomogeneities and Fluctuations in a Phase Transition of a Surface Quasi-One-Dimensional System: In/Si(111)

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We report direct visualizations of the fluctuation and condensation phenomena in a phase transition of a one-dimensional (1D) In/Si(111) system using scanning tunneling microscopy. The high-temperature (HT) and low-temperature (LT) phases are found to coexist on the nanometer scale near T_c. Above T_c, 1D LT-phase stripes fluctuate in the HT phase and coalesce into 2D islands with decreasing temperature. They condense to make the LT phase below T_c. Small areas of the HT phase also exist below T_c. The observed temperature-dependent evolution of the nanoscale inhomogeneities is consistent with the theoretical predictions for a second-order phase transition.

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The coexistence of different phases is one of the intriguing aspects of the phase-transition phenomena. It is due to the competition of phases, which alone dominate at the opposite sides of the phase transition driven by variables such as temperature, chemical doping, magnetic field, etc. Fluctuations as well as condensations of the broken-symmetry phase also constitute interesting topics. Theoretically, such critical behaviors near the phase transition have been extensively studied in statistical physics. In experiments, they have been mostly studied with k-space scattering techniques and macroscopic measurements of the thermodynamic and transport quantities. Recently, real-space observations were made for strongly correlated electron materials, reporting the inhomogeneities (phase separations) in both submicrometer and nanometer scales [1–3].

Another class of materials for which the coexistence of different phases is relevant is those of quasi-one-dimensional (quasi-1D) systems, which are subject to the charge density wave (CDW) instability. Recently, several CDW systems have been found at surfaces [4–7]. Because of the reduced dimensionality, the surface CDW is subject to enhanced fluctuations compared with the bulk CDW, resulting in larger deviation from the mean-field (MF) behavior. The surface CDWs provide better opportunity for the real-space investigation of the phase mixture because the atomic imaging capability of the scanning tunneling microscope (STM) is directly applicable.

In this Letter, we report direct visualizations of the fluctuation and condensation phenomena and their dynamics in a surface quasi-1D system, where the CDW transition was proposed, revealing in unprecedented detail an atomically resolved real-space image. An In/Si(111) surface with one monolayer of In [8,9] undergoes a transition from a high-temperature (HT) 4×1 phase (4×1-HT) into a low-temperature (LT) 8×2 phase (8×2-LT) at about 130 K [7,10–12]. Previously, we reported that this structural transition is not only intertwined with but separable from the metal-to-semimetal electronic transition by having a third nanophase (semimetallic 4×1) at intermediate temperatures from 90 to 145 K [13]. The nanophase occupies less than 5%, and thus we focus here only on the HT and LT phases. Near the phase-transition temperature ($T_c \sim 125$ K) [14] we observed nanoscale inhomogeneities that are dynamic on a time scale visible with STM. Above T_c, 1D stripes with the LT-phase symmetry fluctuate and coalesce to form 2D islands within the 4×1-HT host phase. The 1D stripes are interpreted as fluctuating CDWs of the 8×2-LT phase. Below T_c, moving 2D clusters of the 4×1-HT phase coexist with the overall 8×2-LT phase. The 4×1-HT areas move and change shape, often resulting in concerted shifts of the lattice displacements along the row in the 8×2-LT region. The length change of the 1D 4×1-HT segment accompanied by such concerted shifts in the 8×2-LT region is interpreted to be due to moving solitons.

The experiments were carried out in an ultrahigh-vacuum chamber equipped with variable-temperature STM (Omicron Inc.). The 4×1-HT phase of the In/Si(111) surface was prepared by deposition of In from a Ta-wrapped In source on a Si(111) substrate heated at about 670 K, and verified using STM at RT. The sample was cooled on the STM stage by using a continuous flow cryostat. The STM images were obtained at various temperatures stabilized by controlling the flow.

Figure 1 shows two consecutive STM images (a) and (b) taken at 130 K (slightly above T_c). At this temperature, the 4×1-HT and the 8×2-LT phases coexist with small regions of the 8×2-LT phase embedded within the overall 4×1-HT phase. In the 8×2-LT regions, two 4×2 chains [denoted as A and B in Fig. 1(c)] with bright protrusions tilting in different directions alternate without exception to produce a perfect interchain $8\times$ periodicity. There is an obvious electronic difference in the two phases as seen in the brightness and the I-V curves near zero bias [Fig. 1(d)] [13]. A significant observation is that locally

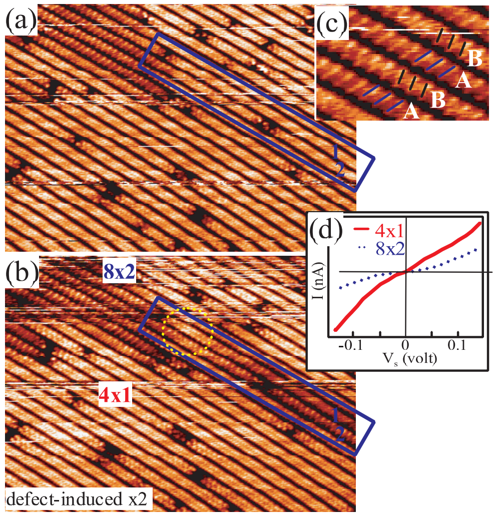

FIG. 1 (color online). (a),(b) Two consecutive STM images taken in 2 min at $T_s \sim 130$ K ($V_s = -0.8$ V). The 4×1-HT and the 8×2-LT coexist. In the boxed area, a change of 4×1-HT into 8×2-LT occurs in rows without (row 1) or with (row 2) defects. (c) A magnified image of the 8×2-LT region showing the two 4×2 chains with different tilting (designated as A and B). (d) I-V curves taken from the two phases.

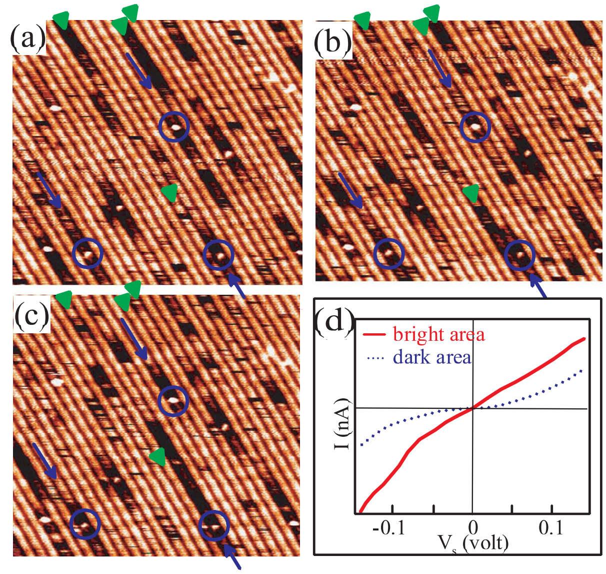

FIG. 2 (color online). (a)–(c) A series of STM images over the same area taken sequentially in a time interval of ~2 min, at $T_s \sim 140$ K ($T_s > T_c$) ($V_s = -0.5$ V). The 1D dark stripes, either captured by defects (circled) (arrows) or existing in the defect-free region (arrowheads), are dynamic. (d) I-V curves taken from the bright region and dark stripes, respectively.

there is a fluctuation in the coexistence of the two phases. Small areas of the 4×1-HT phase convert into the 8×2-LT phase in the successive STM image (see the boxed area). This sudden development of the 8×2-LT phase occurs in both rows with and without defects. It should be noted that $\times 2$ modulations also occur near the vacancies in the 4×1-HT area. However, the vacancy-induced $\times 2$ phase, being as bright as the vacancy-free 4×1-HT phase, is undoubtedly discriminated from the 8×2-LT phase [15].

The development of the LT phase within the 4×1-HT phase also occurs at higher temperature, but in the form of 1D stripes. Figure 2 shows a series of images taken successively from the same area at $T_s \sim 140$ K, well above T_c. At this temperature, the 4×1-HT phase dominates the surface with some isolated, dark 1D stripes. The darkness of the 1D stripes is reminiscent of that of the 8×2-LT phases in Fig. 1. The $\times 2$ structure is observable in some of the dark stripes and not in others. The I-V curves for both types of the stripes are similar, and show a significant reduction in DOS(E_F) from that of the 4×1-HT phase [Fig. 2(d)]. This indicates that the dark 1D stripes belong electronically to the 8×2-LT phase, or at least are precursors bearing its nature.

The dark 1D stripes move and change their lengths on a time scale visible with the STM. Some dark stripes appear tied to bright isolated defects, while their lengths fluctuate continually [see arrows in Fig. 2(a)]. Other stripes, mostly in the defect-free region, suddenly appear and disappear in a chaotic pattern [see arrowheads in Fig. 2(a)] during the scanning time interval (~2 min). Frequently, the changes in brightness at both ends of the dark 1D stripes are abrupt. This indicates that the dynamics of the dark 1D stripes at this temperature is much faster than the line-by-line scanning speed (the advancing speed along the row is approximately a few Å/sec) [16].

It is known that the Peierls CDW phase transition in quasi-1D systems occurs at T_c, which corresponds to the 2D ordering transition temperature (T_{2D}) for surface systems. The temperature range between T_c and T^{MF}, the MF transition temperature, is characterized by fluctuations. For this In/Si(111) system, T^{MF} (~ 430 K) is estimated from the MF relation $2\Delta = 3.5 k_B T^{MF}$ [17] and the zero-temperature CDW gap ($2\Delta \sim 150$ meV [7,12]). Thus the temperature regime below $T^{MF} \sim 430$ K and above $T_{2D} = T_c \sim 125$ K is considered as the fluctuation regime. Therefore, the moving dark 1D stripes in Fig. 2 are interpreted as the fluctuating 1D CDWs. They are not yet condensed by the lateral interchain interaction and show dynamic behavior with a finite correlation length. Some of the fluctuating 1D CDWs are captured by the defects and become less mobile. Upon further cooling, the fluctuating 1D CDWs start to interact with others in the neighboring chains and condense into clusters of the 8×2-LT phase as seen in Fig. 1.

When the temperature is lowered below T_c, the 8×2-LT phase becomes dominant as expected. Figures 3(a)–3(d) show a series of the images taken successively from the same area at 115 K. In these images, bright areas of 2D clusters exist in a dark background 8×2-LT phase. The bright region has $\times 1$ periodicity along the

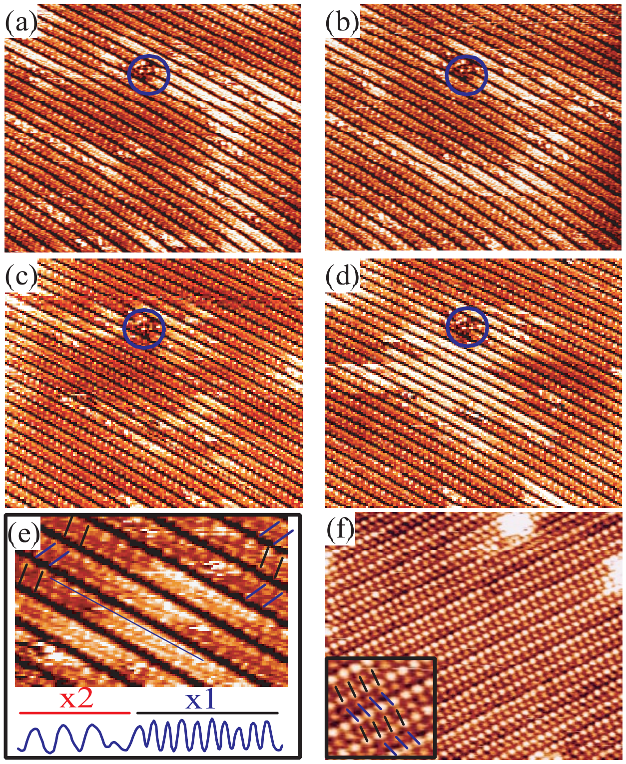

FIG. 3 (color online). (a)–(d) A series of STM images over the same area taken successively in a time interval of ~2 min, at $T_s \sim 115$ K ($T_s < T_c$). The circles are marked to indicate the same positions. (e) A magnified view showing both the 4×1-HT and the 8×2-LT regions with atomic resolution ($V_s = -1.7$ V). (f) STM image taken at $T_s \sim 70$ K ($V_s = +0.5$ V) showing a complete 8×2-LT phase (inset: a magnified image).

chain, indicating that it belongs to the HT phase [see Fig. 3(e)]. These bright 4×1-HT areas are not stationary with time. They fluctuate in size, location, and shape during the scanning time interval, continually varying their boundaries. Defects are frequently, but not always, found near the bright region. It suggests an influence of defects at this temperature against the condensation into the 8×2-LT phase. It seemingly differs from the pinning of the 1D CDW at a temperature above T_c. The detailed roles of defects at different temperatures need further studies.

The bright 2D clusters are ensembles of 1D segments. Each of these 1D segments separates into two dark 4×2 segments in a row. The bright 2D clusters move on an atomic scale by changing the lengths and positions of the constituent 1D segments. The movements of adjacent neighboring 1D segments are coupled, or they would wander off destroying the 2D island. The resulting motion of the bright clusters is rather continuous, in contrast to the chaotic motion and the abrupt boundary of the dark 1D stripes at $T_s > T_c$ observed in Fig. 2.

Figure 3 indicates that there are 2D clusters of the 1D HT segments surrounded by regions of the 8×2-LT phase. Figure 1(c) illustrated that the 8×2-LT phase is made up of 4×1 rows with a stacking sequence of $ABAB$. Therefore each 1D HT segment in Fig. 3 should connect a A row with a A (or A', which is the same as A but shifted by $1a_0$ along the row) row in the global 8×2-LT surrounding phase. Figure 4(a) shows this behavior and the time evolution of the boundary. The 4×1 1D segments move and change their length, but there never is a situation where the left hand and right hand termination in the 8×2-LT phase changes from A to B or B to A. But Fig. 4(b) shows that occasionally something quite different is observed. A 1D 4×1-HT segment is terminated on one side by A and on the other by B. This means that either the 2D 4×1-HT cluster should form a closed loop enclosing an isolated 8×2-LT region or there must be domain boundaries somewhere in the 8×2 region. Observation of the domains of Fig. 4(a) has already been reported [7,13], but the domains of Fig. 4(b) are for the first time identified in this work. These domains are responsible for the half-order streaks observed in diffraction [7,18].

The moving 1D 4×1 segments frequently change their lengths. Occasionally, the length change [for example, even → odd or odd → even change in Fig. 4(a)] is accompanied by a reversal of the displacements of all lattice atoms within the adjoining 4×2 chains. As a result, a concerted shift of the $\times 2$ features by $1a_0$ occurs [see the changes in the right domains in Fig. 4(a)], maintaining the 4×2 chain in the same type (for instance, $A \rightarrow A'$). The resulting registry relative to the neighboring chains alters, while the transverse ordering of $\cdots ABA(')B \cdots$ between the 4×2 chains remains unchanged. On the other hand, transformation of one type of the 4×2 chains to the other type [A to B (or B') or vice versa] by the motion of the 4×1 segment has never been observed. Therefore, it is concluded that the perfect $8\times$ interchain ordering is always maintained despite the existence of dynamically varying

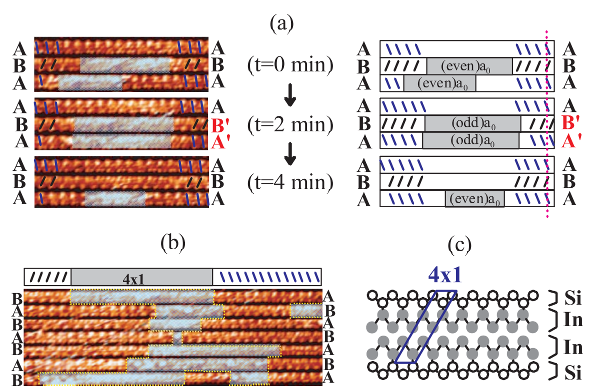

FIG. 4 (color online). The 4×1 segments connecting either (a) the same type or (b) different types of the 4×2 chains in a single row. In (a), the motion of the 4×1 segments induces a concerted shift of the $\times 2$ protrusions (see the changes, $A \rightarrow A' \rightarrow A$ and $B \rightarrow B' \rightarrow B$, indicated by a dotted line in the schematic illustrations). (c) A top view of the In/Si(111)-4×1 structure.

4×1 segments. This agrees with the results of the surface x-ray diffraction study [18].

The concerted shift of the 4×2 chain by $1a_0$ due to the movement of the 4×1 segment in Fig. 4(a) could be interpreted in terms of moving solitons [19]. A soliton is a local phase-slip center connecting two 1D CDW domains with a phase shift of 180° [20]. The displacements of the lattice or charge density variations from the undistorted $\times 1$ positions change signs across a single soliton. According to such a concept of the soliton, the concerted shift of the 4×2 region by $1a_0$ is caused by a passage of a soliton. Then the adjoining 4×1 segments show the even → odd or odd → even change in length by addition or subtraction of the soliton. The 4×1 segments visible in Fig. 4(a) show such changes. We note that similar STM features were also observed at 6 K and interpreted as the soliton dynamics [19]. The problem with this argument is that solitons are a one-dimensional concept and the observed clusters are truly two dimensional. We presume that the 1D solitons in neighboring rows could be coupled to result in 2D clusters by an unknown mechanism.

Both above and below (but close to) T_c, the 4×1-HT and the 8×2-LT phases of In/Si(111) coexist in a *nanometer scale.* This nanoscale inhomogeneity near T_c is a typical phenomenon of a second-order phase transition, as observed in Monte Carlo simulations [21]. Like most of the prior studies, we assume a CDW transition for the In/Si(111) system. The Peierls CDW transition is normally regarded as a second-order transition, as reported for a number of bulk quasi-1D materials [22]. The nanoscale mixture of the HT and the LT phases observed in this work is also compatible with a second-order CDW phase-transition scenario for this surface quasi-1D system [23]. Below T_c, the relative area of the 4×1-HT phase increases with increasing temperature [13]. Proliferation of the 4×1-HT clusters leads to the percolative phase transition to the dominant 4×1-HT phase at T_c.

The characteristic STM features observed in this work demonstrate in real space and confirm the theoretical picture of the fluctuations and condensation in the CDW phase transition [17]. Different regimes of inhomogeneity in the phase transition exist for the In/Si(111) surface, being defined by three characteristic temperatures [T^{MF}, T^*, and T_c $(= T_{\mathrm{2D}})$]. Below T^{MF}, the 1D CDW fluctuations occur (Fig. 2), and then change over to the 2D fluctuations (see Fig. 1) upon cooling. The crossover temperature T^*, which is somewhat above T_c, separates the 1D and the 2D fluctuation regimes. Below T_c, the surface is dominantly in the 8×2 CDW phase with a long-range order, while the minor 4×1 phase coexists (Fig. 3).

In summary, we demonstrate with unprecedented details the existence and dynamics of the nanoscale inhomogeneities in the surface 1D CDW system using STM. This real-space visualization is a direct confirmation of the predicted phenomena of the phase transition near T_c. We envision that the real-space study using STM helps to extract versatile information of the critical phenomena in the structural phase transitions, including dynamics and the influence of defects.

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