Atomic-Scale Phase Coexistence and Fluctuation at the Quasi-One-Dimensional Metal-Insulator Transition

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Scanning tunneling microscopy of a quasi-one-dimensional (1D) metal-insulator transition in an In nanowire array on the Si(111) surface reveals unprecedented details in the transition dynamics. The transition proceeds in microscopic first order, namely, through the domain-by-domain conversion at the nanoscale, from the metallic to the insulating phase or vice versa. The definition of domains and their effective transition temperatures (T_c) are strongly correlated with the distribution of defects. Below T_c, the condensation and the fluctuation of 1D charge density waves are observed within the isolated metallic domains, as well as at the domain boundaries. The appearance of such isolated condensates suggests a strong intrawire coupling: a manifestation of the 1D nature of the critical fluctuation, as well as the origin of the first-order transition.

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Thermal fluctuation is an intrinsic part of a phase transition process. How the fluctuation behaves near critical temperature (T_c) distinctly depends on the nature of phase transitions. Although phase transitions have been studied rigorously up to now, atomistic details of the transitions have not been accessible until recently, in particular, regarding the intrinsic fluctuations and the condensations, and their interactions with the extrinsic disorders [1]. The fluctuation may preclude the development of a long range order at a finite temperature, and random disorders such as impurities and defects may cause the pinning of particular phases nearby, effectively shifting T_c. The effects of fluctuations and disorders in the phase transitions become more important, even dominating, at low-dimensional systems [2].

In this Letter, we report on the observation of the atomic-scale phase coexistence and the fluctuation in a quasi-1D phase transition. The specific system under study is a metallic indium nanowire array self-organized on the Si(111) surface, which undergoes a reversible metal-insulator transition (MIT) of a Peierls type [3]. A Peierls type MIT is driven by the intrinsic instability of a low-dimensional ''metallic'' phase. The ground state is characterized by a charge density wave (CDW) or a periodic charge density modulation coupled with a periodic lattice distortion and by an energy gap across the Fermi level ($2\Delta \sim 100$ to 300 meV for the In nanowires) [3–6].

A huge amount of theoretical and experimental effort has been devoted to the study of the Peierls transitions [2]; however, no real-space observation of any intrinsic fluctuations or their critical behaviors at atomic scale has been reported to date. This is partly due to the fact that most of the Peierls or CDW systems are found in bulk materials [7–10], making any real-space study often difficult to perform. In this regard, a surface system would provide an ideal platform to study, although the surface metallic systems with such Peierls instability are rare with only a few recent exceptions including the In nanowires [3,11–13].

Our present work shows that a seemingly continuous phase transition of In nanowires is actually composed of nanoscale first-order phase transitions whose effective T_c's are influenced by the defect distribution. Furthermore, it reveals, for the first time, the initial condensation and fluctuation of CDW's, and the anisotropic growth of phase correlation in atomic scale.

The sample was prepared by *in situ* deposition of In from a Mo crucible onto a well ordered Si(111)-(7×7) surface at 700 K [6]. The STM head including the sample was cooled fully enclosed within dual cryoshields for the thermal stability, and maintained at a specific temperature over 10 h for the full thermal stabilization before any measurements. The temperature could be controlled by a joule heater with a 0.01 K stability. All measurements were performed under 2×10^{-11} mbar. Low energy electron diffraction (LEED) data were collected in a separate chamber using a CCD camera.

The indium nanowire is composed of two zig-zag In atomic chains and separated by Si atomic chains with a total width of 1.3 nm [14]. At room temperature (RT), the wires are quasi-1D metals longitudinally with a (4×1) periodicity [15,16] as shown in the upper inset of Fig. 1(a). At low temperature (LT), the metallic phase transforms into a CDW phase through a periodicity-doubling along the wires (''$\times 2$'') and across the wires (''$\times 8$'') due to a finite interwire coupling, as shown in the lower inset of Fig. 1(a) [3,17]. The existence of the MIT has been verified by a wide range of experimental methods such as angle-resolved photoemission [3,4,18,19], surface conductivity measurements [5,20], and scanning tunneling spectroscopy [6]. As shown in Fig. 1(c), the temperature-dependent intensities of LEED spots corroborate this picture as well. The data indicate the gradual developments of both

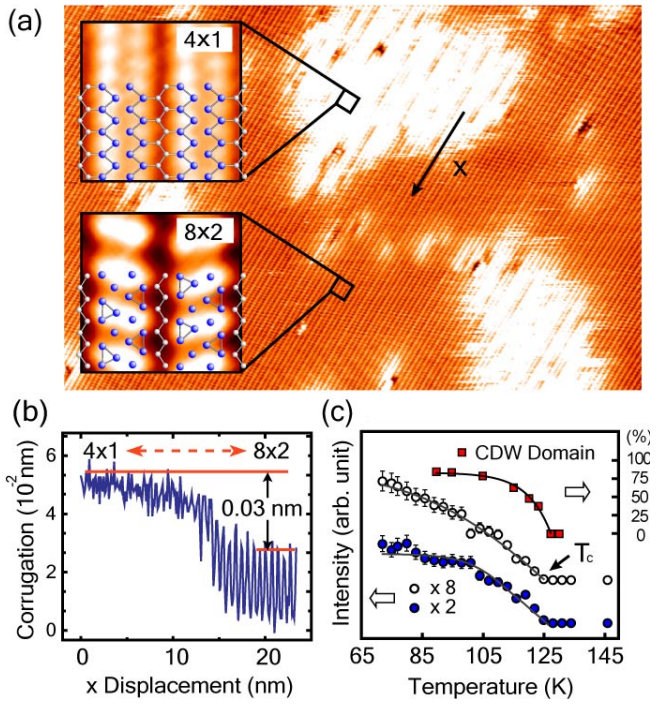

FIG. 1 (color online). (a) Constant current STM images of quasi-1D In nanowires obtained at various temperatures. Upper and lower insets are RT (4×1) and LT (8×2) phases with corresponding structural models [6,17], while the large-scale image is a mixture of two phases coexisting in nanoscale domains. All images were taken at 121.0 K ($\sim T_c$), with the sample bias of -0.7 V and the tunneling current of 100 pA. The insets are 5×5 nm^2 and the full image 150×100 nm^2. (b) A line profile across the two different domains along the nanowire as indicated by "x" in (a). (c) Temperature-dependent intensities of LEED spots of transverse ($\times 8$) and longitudinal ($\times 2$) orders (lower two curves) and normalized integrated LT (8×2) area in STM images (top curve). The macroscopic T_c is indicated by an arrow.

$\times 8$ and $\times 2$ orders, and hence a macroscopically continuous phase transition with the onset of $\sim$125 K, i.e., T_c.

Surprisingly, however, the STM imaging of the system below T_c reveals two types of distinct domains coexisting, as shown in Fig. 1(a): Domains of RT (4×1) and LT (8×2) CDW phases appear bright and dark, respectively. Scanning tunneling spectroscopy measurements on each domain show that the domains of the (4×1) phase are metallic, while those of the (8×2) phase insulating with an energy gap, in agreements with the previous work [6]. A line profile of the STM image across the domain boundary indicates, as shown in Fig. 1(b), the apparent height difference between the two domains is about $\sim$0.03 nm. This difference is not surprising, in view of the large difference between two phases in the electronic density of states near the Fermi level, which plays a dominant role in tunneling. Indeed previous surface x-ray diffraction study found no significant geometric height difference between the RT and LT structures [17]. Thus the domain contrast in the STM images, i.e., the apparent height difference is attributed mainly to the electronic origin, not a geometric effect.

Upon further cooling, the metallic (4×1) domains were converted into the insulating (8×2) ones. Figure 2 shows a typical example of how the transition proceeds below T_c. Triggered by a minute temperature drift or fluctuation, the conversion of a large area from the metallic to the CDW phase occurred suddenly, leaving patches of smaller metallic domains. Thus the phase transition is of first order, advancing domain by domain. The smaller the domains were, the lower the temperature at which the conversion occurred. This is further supported by the data of the total area of the CDW domains identified in STM images as a function of temperature [uppermost plot of Fig. 1(c)]. It shows a continuous increase of the total area of CDW domains similar to that of the LEED intensities, demonstrating the coexistence of the metallic and the CDW domains in the range of 100–125 K.

A careful examination of Figs. 2(a) and 2(b) reveals that every metallic domain is associated with defects at its boundary, as marked by the arrowheads. Thus the stability of metallic domains below T_c can be persuasively attributed to the presence of defects. Close-up views of these defects show their interaction with the CDW phase. Defects or steps can easily destroy the glide symmetry of the LT (8×2) CDW phase in the direction perpendicular to the indium wire [17]. Such an interaction induces locally (4×2) structures in neighboring wires, or along the same wires as shown in the insets of Figs. 2(a) and 2(b) [6,21]. These defects induce a strong lattice distortion and hinder the formation of the charge ordering or CDW state near the defects [6]. These observations suggest that the defects are repulsive to the CDW state. Then, if the defects are located close to each other, they would form repulsive barriers to the CDW phase, providing relative stability to the metallic

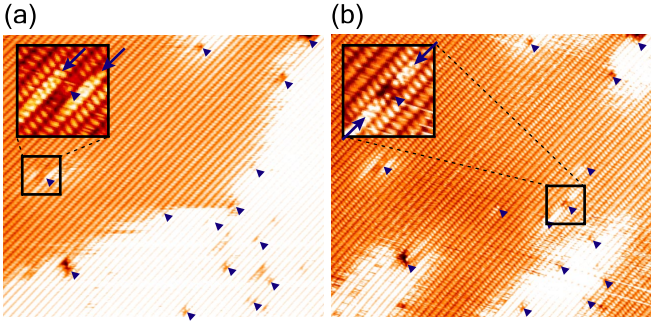

FIG. 2 (color online). (a)–(b) Sequential STM images showing large-scale domainwise fluctuations at 123.0 K. The positions of defects are indicated by triangular arrowheads. The insets are the close-up views of defects, which locally induce (4×2) structures (a) in neighboring rows pointed by two arrows or (b) along the same nanowire. Images are 60×60 nm^2 obtained at the sample bias of -0.7 V and the tunneling current of 100 pA.

phase. Thus the entire surface would be divided into domains of different sizes and thereby different effective T_c by the random distribution of defects and steps [22,23].

The role of defects is also apparent in Fig. 1(c). The growth of the (8×2) CDW area is close to saturation at $\sim$100 K, with $\sim$85% of the total area converted. The unconverted areas are due to mostly the (4×2) structure locally induced by defects and steps as described above. Since these structures are already in $\times 2$ order longitudinally, any further conversion contributes only to "$\times 8$" order in LEED, but not to "$\times 2$." Thus the contrast between the saturation behaviors of two LEED spots in Fig. 1(c) is consistent with the STM data.

While some areas pinned down by defects are broken into (4×2) structures, areas away from defects exhibit the dynamic fluctuation. As shown in a temporal series of images in Figs. 3(a)–3(c), within a metallic domain, several short, dark and fuzzy segments differentiated from the surrounding (4×1) phase were found in individual nanowires. These short segments are not static but fade, emerge, and move randomly along the wires. No defects were found within the domain that may possibly be related to such fluctuations. Occasionally, some of the fluctuating segments revealed the clear CDW-like order which is similar to those at the LT ground state, as marked by the dotted ellipse in Fig. 3(b). Furthermore, no such anisotropic 1D fluctuations were observed *above* T_c. Thus these can be convincingly attributed to the phase instability due to thermal perturbation below T_c. In this sense, such a local 1D charge ordering represents an initial stage of the CDW condensation and fluctuation, to our best knowledge, observed for the first time at atomic scale [2].

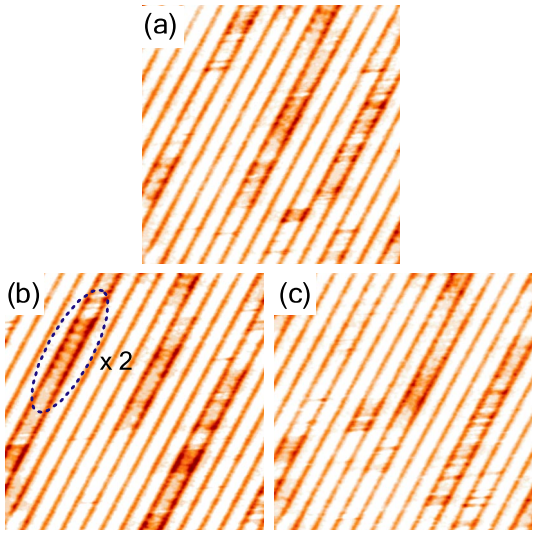

FIG. 3 (color online). (a)–(c) A temporal series of STM images of the same area of a metallic domain at 121.0 K that exhibits fluctuating short 1D segments. A dotted ellipse in (b) denotes the transient condensation of $\times 2$ orders. Image sequences are separated by 2 min. Images are 18×18 nm^2 in size. The sample bias is -0.5 V and the tunneling current 50 pA.

It is emphasized that the initial CDW condensates are always transversely intervened by (4×1) metallic wires, as shown in Fig. 3. That is, no pairs of the CDW condensates fluctuating next to each other were observed in metallic domains, although the average spacing between the CDW condensates decreased until the sudden domain-wide conversion to the CDW phase occurred. This suggests that there exists a short-range repulsive potential between the CDW condensates. The domain-wide conversion is then the process of surmounting the potential barrier to the minimum free energy state of the fully interlocked CDW phase. If this is indeed the case, then the interwire coupling may be the origin of the first-order character of the present transition.

Since T_c is specific to each domain, presumably dependent on the pinning defect distribution, there is a possibility that the observed phenomena in the small metallic domains may be different from those in the larger domains with higher T_c's. However, the observation of the similar fluctuations over a wide range of domains in size from $\sim 6 \times 10^2$ to 3×10^4 nm^2 leads us to believe that the behavior is universal to the domainwise transition of the present system.

The dynamic fluctuation is not just restricted within the metallic domains, but also found at the boundaries between the metallic and the CDW domains. As shown in Fig. 1(b), the spatial change from the metallic phase to the insulating one occurs gradually along each nanowire. A series of STM images shows that these domain walls continually move in 1D along each nanowire: Arrows in Figs. 4(a)–4(d) indicate how the domain walls of three individual wires migrate while converting the metallic wires into the CDW's or vice versa. Despite the finite time resolution of STM scan, it is clearly seen that each nanowire fluctuates individually in 1D as denoted by short bars in Figs. 4(a)–4(d). At the same time, it is also noted that there is some embryonic interwire coupling in the domain wall motion, as denoted by long bars in Figs. 4(c) and 4(d). That is, the two outmost metallic wires show correlated motion. Similar events were frequently observed during STM imaging, where two to five adjacent nanowires exhibit a transversely correlated domain wall dynamics. The qualitative difference between the fluctuation modes of inner areas of domains and domain boundaries is ascribed to the transverse couplings provided by the background phase.

We note that, in addition to the fluctuations in the MIT described so far, there exist 1D fluctuations intrinsic to the CDW state [3,6]. These fluctuations are also significant near T_c within the CDW condensates as well as in the CDW domains [6]. Such fluctuations would reduce LT (8×2) orders in LEED. Thus the steeper rise in the total area of the CDW phase compared to that of the LEED

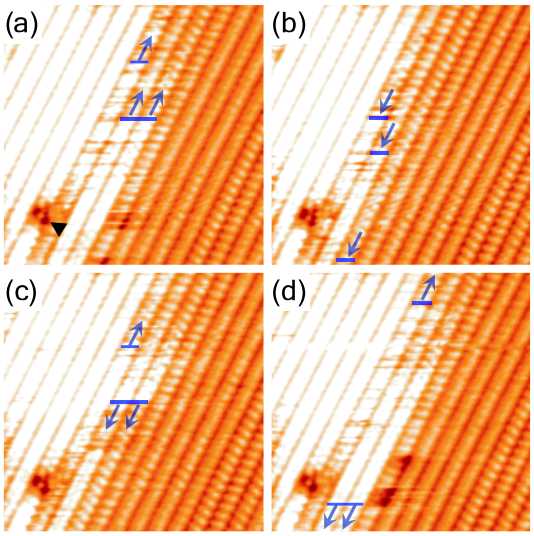

FIG. 4 (color online). (a)–(d) A temporal series of STM images of the interface area between metallic and CDW domains at 121.0 K. Arrows and bars indicate the atomic-scale motion of domain walls. The arrowhead in (a) denotes an immobile ''marker'' vacancy defect. Images are 18×18 nm^2 in size with the sample bias -0.7 V and the tunneling current 50 pA.

intensities in Fig. 1(c) can be ascribed to the influence of these fluctuations, because the fluctuations would predominantly affect the CDW states.

Our data thus far show that the otherwise sharp first-order phase transition is smeared out by the distribution of nanoscale domains having their own unique T_c's influenced by pinning defects. Such strong influence of microscopic inhomogeneity to a first-order transition had been asked earlier by Imry and Wortis [22]. A subsequent rigorous mathematical theorem [24] states that for a low-dimensional system (dimension $d \leq 2$), the minimum free energy state is always unique for the nonzero concentration of impurities. This was interpreted that there can be no phase coexistence and hence no latent heat, with the first-order transition smeared out [25]. The present STM work, however, shows that the first-order transition persists at nanoscale, with the transition proceeding domain by domain.

A recent experiment on the surface conductivity of the present system using a microscopic four-point probe method revealed strong intrinsic nonlinear conductivity near T_c [5], while no such nonlinearity was observed away from the T_c regime. We speculate that this nonlinearity is related to the coexistence of metallic and CDW domains constituting percolative networks near T_c. It would be fruitful further to pursue experimental and theoretical understandings in this area.

In summary, our present study shows that, in a quasi-one-dimensional system of In nanowire arrays, the phase transition proceeds locally domain by domain, not in a truly continuous manner. The fluctuation modes near T_c inside and outside the domains are identified in atomic scale, from which the novel 1D nature of the critical fluctuation and the interwire coupling are elucidated. The initial anisotropy in phase correlation is consistent with the CDW mechanism with a finite interwire coupling. Our findings should be applicable to a wide range of low-dimensional MITs.

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[1] L. Petersen, Ismail, and E. W. Plummer, Prog. Surf. Sci. **71**, 1 (2002).
[2] G. Grüner, *Density Waves in Solids* (Addison-Wesley, Reading, MA, 1994).
[3] H. W. Yeom *et al.*, Phys. Rev. Lett. **82**, 4898 (1999).
[4] J. R. Ahn *et al.*, Phys. Rev. Lett. **93**, 106401 (2004).
[5] T. Tanikawa, I. Matsuda, T. Kanagawa, and S. Hasegawa, Phys. Rev. Lett. **93**, 016801 (2004).
[6] S. J. Park, H. W. Yeom, S. H. Min, D. H. Park, and I.-W. Lyo, Phys. Rev. Lett. **93**, 106402 (2004).
[7] R. V. Coleman *et al.*, J. Vac. Sci. Technol. A **6**, 338 (1988).
[8] C. G. Slough, W. W. McNairy, R. V. Coleman, B. Drake, and P. K. Hansma, Phys. Rev. B **34**, 994 (1986).
[9] T. Sleator and R. Tycko, Phys. Rev. Lett. **60**, 1418 (1988).
[10] P. Mallet *et al.*, Phys. Rev. B **60**, 2122 (1999).
[11] T. Nakagawa *et al.*, Phys. Rev. Lett. **86**, 854 (2001).
[12] K. Swamy, A. Menzel, R. Beer, and E. Bertel, Phys. Rev. Lett. **86**, 1299 (2001).
[13] J. R. Ahn, H. W. Yeom, H. S. Yoon, and I.-W. Lyo, Phys. Rev. Lett. **91**, 196403 (2003).
[14] O. Bunk *et al.*, Phys. Rev. B **59**, 12228 (1999).
[15] T. Abukawa *et al.*, Surf. Sci. **325**, 33 (1995).
[16] I. G. Hill and A. B. McLean, Phys. Rev. B **56**, 15725 (1997).
[17] C. Kumpf *et al.*, Phys. Rev. Lett. **85**, 4916 (2000).
[18] O. Gallus *et al.*, Eur. Phys. J. B **20**, 313 (2001).
[19] H. W. Yeom *et al.*, Phys. Rev. B **65**, 241307 (2002).
[20] T. Uchihashi and U. Ramsperger, Appl. Phys. Lett. **80**, 4169 (2002).
[21] G. Lee, S.-Y. Yu, H. Kim, and J.-Y. Koo, Phys. Rev. B **70**, 121304 (2004).
[22] Y. Imry and M. Wortis, Phys. Rev. B **19**, 3580 (1979).
[23] P. N. Timonin, Phys. Rev. B **69**, 092102 (2004).
[24] M. Aizenman and J. Wehr, Phys. Rev. Lett. **62**, 2503 (1989).
[25] J. Cardy, Physica (Amsterdam) **263A**, 215 (1999).