Direct Evidence of the Charge Ordered Phase Transition of Indium Nanowires on Si(111)

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A controversial issue of the driving force for the phase transition of the one-dimensional (1D) metallic In wires on Si(111) is studied by low-temperature scanning tunneling microscopy and spectroscopy. The energy gap opening and the longitudinal charge ordering through charge transfer at the Fermi level are unambiguously observed. The vacancy defects induce a local charge ordering decoupled from a lattice distortion above T_c, and pin the phase of charge order below T_c. All these results below and above T_c including the detailed features such as local fluctuations strongly support the 1D charge-density-wave mechanism for the phase transition.

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Self-organized 1D materials have drawn much interest, because of not only ease to fabricate atomic scale structures, but also the richness of exotic physical phenomena they exhibit such as a Jahn-Teller distortion [1], non-Fermi liquid behavior for one-dimensional metallic system [2], and charge-density wave (CDW) condensation due to Peierls instability [3,4], etc.

The (4×1) phase of the Si(111) surface formed by a monolayer of In is a model system of self-organized nanowires exhibiting an 1D metallic character on a surface [5–7]. Recently, this system was reported to undergo a reversible phase transition to a (8×2) phase at about 100 K, which was interpreted as being driven by 1D-CDW formation along the nanowires, since it shows a perfect Fermi-surface nesting with $2k_F = \pi/a_0$ ($a_0 = 3.84$ Å) before the transition and a gap opening accompanied by a periodic lattice distortion (PLD) after the transition [8].

However, the idea of a quasi-1D CDW transition was questioned by a subsequent x-ray diffraction (XRD) experiment. In this study, the fully condensed CDW phase was not observed even at far below the transition temperature (T_c) [9]. Furthermore, a first-principles calculation, which successfully reproduced the atomic and band structures for the room temperature (RT) metallic phase, found no band gap opening for the low-temperature (LT) phase, and argued that the phase transition is simply induced by an energy-lowering lattice distortion [10]. But a recent detailed angle-resolved photoemission (ARP) study [11] confirmed again the band-gap formation during the transition, and suggested that the extra splitting of the In 4*d* core-level at LT could originate from the charge ordering. However, the LT band structure itself, except for the existence of the band gap, is still under debate with unresolved complexities as indicated by another ARP study [12]. In spite of all the complexity presented so far, one central issue in the above debate is definitely the existence of the charge ordering beyond a simple lattice perturbation, which may be probed directly by scanning tunneling microscopy (STM). Although the previous STM images showed clear periodicity doubling along the In nanowires below T_c, high sample bias and no corresponding empty state images made it impossible to determine the gap opening of the metallic states near the Fermi level (E_F) and clarify the origin of the ordering at low temperature [8].

In this Letter, we investigate the temperature-dependent electronic structures of the Si(111)(4×1)-In system with high-resolution STM and scanning tunneling spectroscopy (STS). By comparing STM and STS data for the electronic states near E_F and across T_c, we made crucial discoveries: (i) the phase transition is truly a metal-insulator transition with an energy gap opening and (ii) the low-temperature phase is indeed *charge ordered* along the wires, with the out-of-phase distribution of the occupied and unoccupied states. Our analysis of charge orderings near defects above T_c reveals that a lattice distortion can be distinguished from a charge ordering. A fluctuating charge-ordered state is also found in In wires terminated by two out-of-phase defects. These observations provide the crucial evidence for the CDW ground state.

The sample was made by *in situ* deposition of In from a Mo crucible onto the well-ordered Si(111)-(7×7) surface at 700 K under 1×10^{-10} Torr and subsequently confirmed by low-energy electron diffraction (LEED). The STM measurements were performed under 2×10^{-11} Torr in another chamber. The STM head was cooled by liquid nitrogen and equipped with a joule heater for the temperature control. The experiments were performed at a temperature range of 78–135 K within ± 0.01 K accuracy.

Figure 1 shows the typical high-resolution STM images of the same areas of In nanowires at bias voltages close to E_F, before and after the phase transition. As shown in Fig. 1(c), each In nanowire consists of two zigzag In chains [the longitudinal (x) rows of bright protrusions] separated by one zigzag Si chain (the dark stripe) [7,10]. As marked by circles in Figs. 1(a) and 1(b),

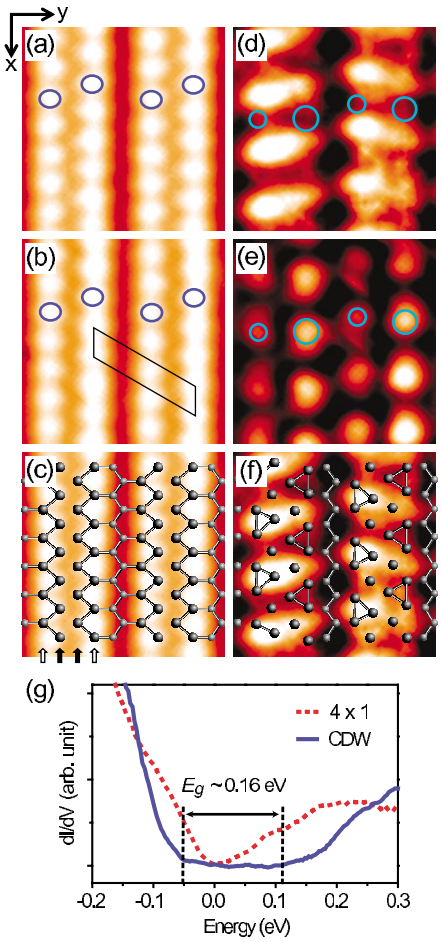

FIG. 1 (color online). (a) Filled and (b) empty state STM images taken at 135 K using a dual scan mode, and similar images (d),(e) at 78 K. The same image (c) as (a) and (f) as (d) with the (4×1) and (8×2) structure models superimposed on [7,9]. (g) Derivative of I-V spectra averaged over 20 points before (dashed line) and after (solid line) the phase transition. Open circles in (a),(b),(d),(e) mark charge-density maxima in empty state images. A parallelogram in (b) denotes a (4×1) unit cell. The imaging conditions are ∓ 0.15 V and 20 pA for (a) and (b), and ∓ 0.30 V and 30 pA for (c) and (d), respectively.

the maxima of both filled and empty states of the RT (4×1) phase are found at the same locations at very close to E_F, indicating its gapless nature. The metallic nature is confirmed quantitatively by the STS measurement [Fig. 1(g)] [6]. These maxima correspond roughly to the two inner In atoms [indicated by black arrows in Fig. 1(c)], which are the major contributors to the metallicity of the In wires [10,11].

As the temperature is lowered below T_c ($\sim$130 K), the local charge densities are drastically redistributed as shown in Figs. 1(d) and 1(e). Most of all, the periodicity is doubled both in a longitudinal ($\times 2$) and a transverse ($\times 8$) direction with breaking the symmetry into the glide one. The filled-state image is basically similar to that of the previous report taken at a much higher sample bias ($\sim$2.0 V) [8]. However, the charge-density maxima in filled and empty states at energies similar to those of Figs. 1(a) and 1(b) are *completely out of phase* with each other along the wires. Bulk materials with 1D CDW characters such as $K_{0.9}Mo_6O_{17}$ and η-Mo_4O_{11} exhibit similar out-of-phase charge ordering, as well as a gap opening across E_F [13,14]. Indeed, the band-gap opening is clearly confirmed by STS as shown in Fig. 1(g). The size of the energy gap $\sim$160 meV is quantitatively consistent with the previous ARP results [8,11].

It should also be mentioned that the above STM images for the LT phase do not match the calculated ones based on the energy-optimized PLD [10]. In particular, the calculation does not reproduce the out of phaseness between the empty and filled states, as it fails to produce a gap opening at E_F. The STM image calculation was done with energy integration up to 1 eV from E_F and our experiment indicates that the STM images shown above are basically the same up to ± 1.0 V. Only the empty state images obtained above $+1.0$ eV (images not shown) are similar to the simulated one. The failure of the theoretical calculation based on local-density approximation for the LT phase is significant, in strong contrast to its success in describing the RT metallic phase [15–17]. In Fig. 1(f), we suggest one of the possible but tentative correlation of the charge-ordered states with the underlying lattice using the structure model of the (8×2) obtained recently by an XRD study [9]. Detailed bias dependent analysis of the STM images will be published elsewhere [18].

The facts (i) that there exist a clear charge ordering through charge transfer and an energy gap across E_F, and (ii) that the energy-optimized PLD calculation does not reproduce the charge ordering suggest strongly that the LT ground state is a CDW state. A similar charge ordering together with a PLD may be also observed in a systems with a Jahn-Teller distortion as realized in the Si(001) surface. However, such a mechanism is clearly incompatible with strongly dispersing half-filled 1D metallic bands of the In wires observed by the ARP experiments [11]. The CDW nature of the present system beyond a simple lattice distortion is further corroborated from the study of the local fluctuations as discussed below.

A charge ordering may be induced by steps or defects above T_c [19]. As shown in Fig. 2(a), among the metallic In wires of the (4×1) structure, a noticeably different charge-density modulation is found next to a defect attributed to In vacancies. The modulation is confined along and within a single wire (see the boxed area). In more detail, as shown in Figs. 2(b), 2(c), and 2(e), this local modulation has a periodicity of $\times 2$ and gradually decays away from a defect. The direct comparison of the filled and empty state images of the defect-induced modulation reveals that *the modulation is in phase in the neighboring sites of the defect but gradually becomes out of phase farther away before it decays away eventually.* While the in-phase modulation is straightforwardly thought to correspond to a lattice distortion caused by the defect,

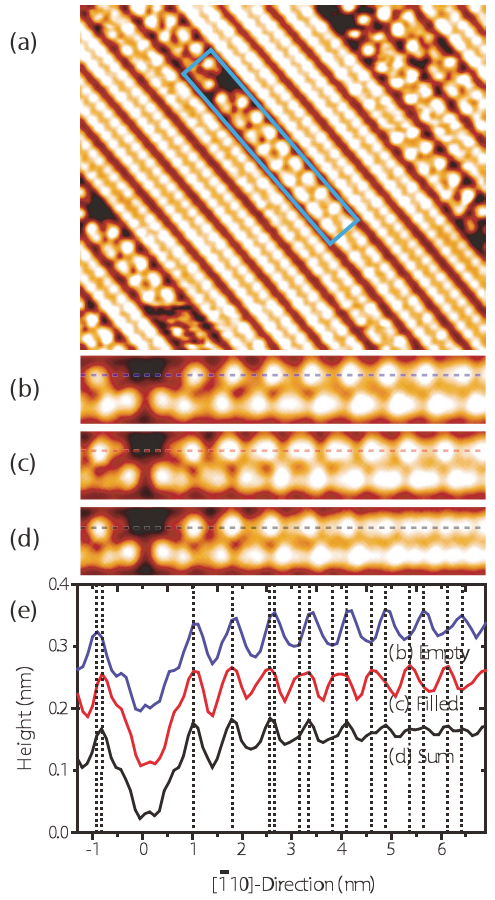

FIG. 2 (color online). (a) Filled-state STM image of a terrace with several In wires and defects at $T = 135$ K. Enlarged images of a box in (a) are (b) empty and (c) filled-state images of an In nanowire including defects, and (d) an image of their arithmetic sum. Line profiles of the upper row of the In nanowire are plotted in (e) for the comparison of the charge redistribution and accompanying PLD. The imaging conditions are ± 0.15 V and 20 pA.

the out-of-phase one is essentially identical to the charge ordering observed below T_c. The gradual buildup of a charge ordering away from a defect is incompatible with a simple lattice distortion, which should decay monotonically from a defect site. This observation manifests that the out-of-phase charge ordering does not owe its existence simply to the lattice distortion although the charge ordering is necessarily accompanied by a "subtle" PLD.

While the vacancy defects can induce the CDW or charge ordering locally above T_c, similar defects can play a different role below T_c. Figure 3 shows a typical empty state STM image of the In nanowires at $T = 78$ K with a few defect sites. It is clear that the (8×2) order is established globally on the surface. As had been noted earlier [9], while each individual (8×2) unit (two In wires) has a long-range order [20], the longitudinal correlation *between* the In wires with the (4×2) structure are weak. This is thought to be due to a glide symmetry intrinsic to this surface [10]. However, parts of some In wires (marked by the black arrows) are not in the definite $(\times 2)$ order along the wires, as shown in the box with "O" in Fig. 3(a), for example. Unlike the normal charge-ordered phases, they look striped with little corrugations. They appear similar also in the corresponding filled-state images (images not shown) as well. Such disordered parts are found to be bound by the defects (dark vacancies in the image) at both ends with no exception. At the same time, although similarly bound by two defects, ones within the box marked by "E" in Fig. 3(a) are not different from the normal charge-ordered In wires. The direct quantitative measurements reveal that those striped chains are found only when the separation between the terminating defects is an *odd* multiple of a_0 as in Fig. 3(b) (black arrows) but those within the box E has a length of *even* multiple of a_0 (white arrows) [21]. That is, In wires terminated by out-of-phase defects have a section of a disorder or fluctuating phase in between. Note that the occurrence of the disorder is purely 1D and is not correlated with the neighboring chains.

We further note that such a disordered segment can be anywhere between the defects, as evident in Fig. 3(b).

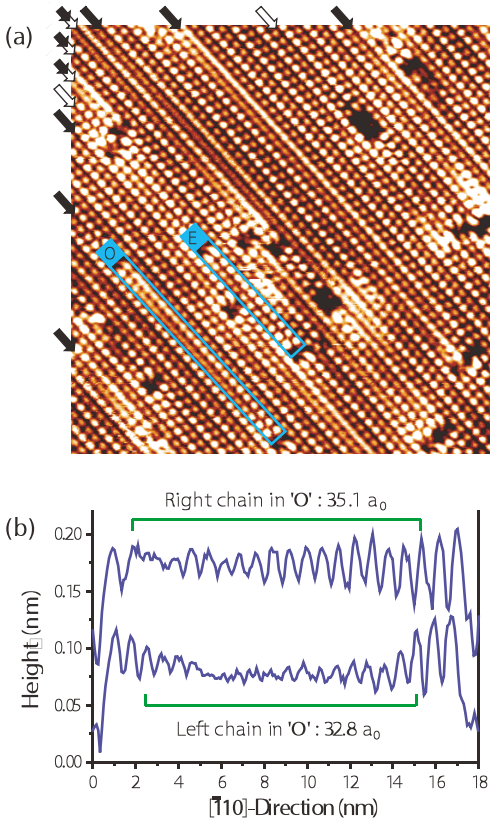

FIG. 3 (color online). (a) An 30×31 nm^2 empty state STM image taken at 78 K and (b) line profiles of two chains in a box with O. The box with O contains charge disordered In chains, while the box with E contains normal CDW chains. Black arrows denote disordered chains bound by defects while white arrows ordered chains despite defects. The sample bias and the tunneling current are $+0.6$ V and 0.1 nA, respectively.

Furthermore, the STS measurements at this segment shows an energy gap similar to that of ordered regions (not shown). These detailed properties of the disordered segment are in variance with the picture of a simple lattice distortion, since a lattice distortion (and its phase), which should monotonically decay away from each defect, would locate the disordered part near the center of a wire and at the same time the loss of the $\times 2$ order should close the gap as in the (4×1) phase. We thus interpret the disorder induced by two out-of-phase defects, as a fluctuating "soliton" state of a CDW at the phase boundary [22].

The previous XRD study made an argument against the CDW mechanism of the present phase transition from the observation that the (8×2) superstructure was not fully developed even at 20 K. However, a subsequent first-principles calculation [10] estimated the energy differences between various (8×2) configurations to be much less than that between the (4×2) and the (8×2) phases, and thus expected little correlation among the (4×2) wires. Thus persistent half-order streaks in the reciprocal space reflect disorder in the intrinsic glide symmetry of this system rather than fluctuating CDW states, and it does not contradict the 1D CDW-driven phase transition itself. Our temperature-dependent STM images and LEED data (data not shown) show that the condensation of the charge ordering begins from $\sim$130 K and fully expands longitudinally and transversely over the entire surface by $\sim$100 K in a microscopic first-order phase transition [22], with the exception of limited regions influenced by surface defects or steps as seen in Fig. 2. As the temperature is lowered below T_c further, the defect-pinned 1D fluctuations as shown in Fig. 3 would gradually be reduced and stabilized to the CDW phase. Thus, although the domain sizes themselves do not vary, defined essentially by the extrinsic defect density, the reduced fluctuation around the defects would increase the (8×2) order and enhance the XRD intensities at LT. This would explain in part why the intensities of the 8th- and 4th-order spots in surface XRD change, while their widths were preserved, as the temperature was lowered [9].

We note that the phase transition of this system qualitatively differs from that of Si(100)-(2×1) to $c(4 \times 2)$ which does not exhibit a "metal-insulator" transition (or more generally a symmetry breaking order-order transition) but an order-disorder transition. A recent debate on the nature of the phase transition of Sn/Ge(111)-$\sqrt{3} \times \sqrt{3}$ to 3×3 also focuses on the distinction between the order-order and the order-disorder transitions, with an emerging consensus that the RT phase is characterized by a fluctuation of a local order, namely, a (3×3) phase [23]. The role of defects in these system is to *pin* the thermal fluctuation in their immediate neighborhoods [24,25], while it is, in the CDW systems such as the present In wires, to *induce* a local order beyond the immediate neighborhoods.

In summary, the 1D metallic In nanowire system is unambiguously shown by high-resolution STM and STS to undergo a gap opening metal-insulator transition with a definite charge ordering, which renders the occupied and unoccupied density of states maxima out of phase with each other. Vacancy defects are found to induce a similar charge ordering above T_c, whose lateral distribution cannot be explained by a simple lattice distortion. In addition, out-of-phase end defects of an In wire separated by an odd multiple of a_0 lead to a 1D charge disordering or fluctuation within. All such experimental findings are consistent with the idea of a CDW-driven phase transition, beyond a simple energy-lowering periodic lattice distortion.

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