PHYSICAL REVIEW B **81**, 075401 (2010)

Controlled electron doping into metallic atomic wires: Si(111)4×1-In

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(Received 12 November 2009; revised manuscript received 4 January 2010; published 1 February 2010)

We demonstrate the controllable electron doping into metallic atomic wires, indium wires self-assembled on the Si(111) surface, which feature one-dimensional (1D) band structure and temperature-driven metal-insulator transition. The electron filling of 1D metallic bands is systematically increased by alkali-metal adsorption, which, in turn, tunes the macroscopic property, that is, suppresses the metal-insulator transition. On the other hand, the dopant atoms induce a local lattice distortion without a band-gap opening, leading to a microscopic phase separation on the surface. The distinct bifunctional, electronic and structural, roles of dopants in different length scales are thus disclosed.

DOI: 10.1103/PhysRevB.81.075401 PACS number(s): 73.20.At, 68.35.Rh, 68.37.Ef, 73.22.Gk

One important issue for practical applications of nanomaterials is the systematic control of their electronic properties through, for example, doping impurities. Thus, in recent years, atomic and molecular doping techniques have been intensively studied for semiconductor nanodots/nanowires and carbon-based nanomaterials, which often led to drastic changes in their physical and chemical properties.[1–5] In particular, doping metallic nanowires is very interesting also in fundamental points of view, since dopants can strongly interact with exotic quantum states of one-dimensional (1D) metals such as the non-Fermi-liquid state[6,7] and broken-symmetry states (density waves or superconducting states).[7–9] The microscopic understanding of intriguing interactions of dopants with those quantum states is an important issue not only in nanowires but also in bulk low-dimensional materials.[10–14] However, the systematic and reproducible tuning of the electronic property is still challenging, especially when host structures shrink down to truly atomic or molecular level, where local microscopic interactions of dopants with host wires become crucial.[15,16]

Recently, much attention has been paid to metallic wires with truly atomic dimension, atomic wire arrays on semiconductor surfaces such as In or Au atomic chains self-organized on Si(111) (Refs. 17 and 18) or vicinal Si surfaces.[19,20] Electrons in these systems are well confined within the atomic chains and form rather ideal 1D (quasi-1D) metallic bands. These systems are easily accessible with scanning tunneling microscopy (STM) and thus provide unprecedented possibility to study atomistic details of microscopic interactions in 1D systems. Intriguing phase transitions were found on a few metallic atomic wire systems,[17,19,20] which are commonly accompanied with periodic lattice distortions (PLDs) and band-gap openings, and thus proposed as metal-insulator transitions into charge-density wave (CDW) ground states. The controllable doping to a "metallic" atomic wire system, which is expected to greatly affect the CDW transitions, has not been realized while we recently showed the systematic control of the band-gap size by impurities for Au-induced "semiconducting" atomic wires on Si(111).[18]

In this paper, we exploit the possibility of electron doping into a prototype metallic atomic wire system on silicon, the extensively studied In-induced 4×1 structure on Si(111) (4×1-In hereafter).[17,21–29] The wire is composed of four In atomic rows packed closely between Si zigzag chains as sketched in Fig. 1(a).[21] This system has three quasi-1D metallic bands at room temperature, one of which has a well-nested Fermi surface (FS) with a half electron filling [Fig. 1(b)].[17,24] The surface undergoes a transition into the insulating 8×2 structure at the transition temperature (T_c) of

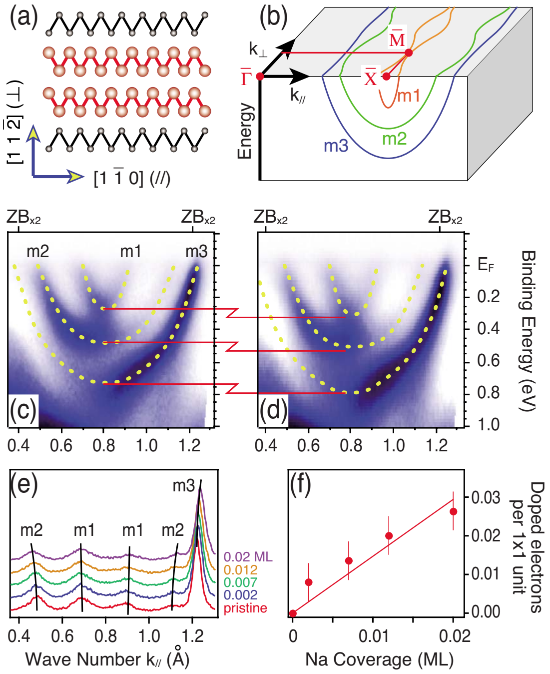

FIG. 1. (Color online) Schematics of the (a) atomic and (b) electronic structures of Si(111)4×1-In. The wire consists of zigzag In rows (large spheres) sandwiched by Si rows (small spheres) on the topmost layer of Si(111). Measured energy bands (ARPES intensity distributions in the energy-momentum space) for the (c) pristine and (d) Na-deposited In/Si(111)-4×1 surface at 300 K. The Na coverage for (d) was 0.007 ML. The slices were taken along the $\bar{\Gamma}$-$\bar{X}$ line of the surface Brillouin zone in (b). The photoelectron intensity is given in a gray scale with darker contrast for higher intensity. (e) and (f) show momentum distribution curves of the ARPES intensity at Fermi energy (E_F) and the amount of the doped electrons estimated from the peak positions of these curves. The line in (f) is linear fit of the plot.

125 K.[17,24–27] We demonstrate that electrons can be systematically doped to the wires by alkali-metal (Na) adsorbates, which globally convert the insulating phase below T_c into metallic. The deposited Na yields a locally distinct PLD (a 4×2 structure) with a reduced *metallic* electron density. That is, the dopants affect the nanowires in two distinct ways, both electronically and structurally, in different length scales.

STM observations were carried out using a commercial variable temperature STM (Unisoku, Japan) at 77–150 K. Angle-resolved photoelectron spectroscopy (ARPES) was performed to map electronic band dispersions at temperatures between 40 and 300 K using a high-performance electron analyzer (R4000, VG-Scienta, Sweden) at the 3A2 beamline in Pohang Acceleration Laboratory (Pohang, Korea) and at the homelab. The total energy and angle resolutions were set better than 40 meV and 0.15°. The sample was prepared by depositing one monolayer (ML) of In onto the Si(111)-7×7 surface at 700 K,[28,29] followed by Na deposition at 300 K from a heated dispenser. A slightly vicinal Si(111) wafer oriented toward $[\bar{1}\bar{1}2]$ was used in the ARPES measurements to make a single-domain surface phase.[29] The Na coverage (Θ_{Na}) was estimated by referring to the well-established phase diagram and the work-function change on Si(111).[30]

We begin with showing how the deposited Na affects the band structure. The triple quasi-1D metallic bands of the 4×1-In surface, denoted as $m1$, $m2$, and $m3$, are shown in the ARPES intensity map of Fig. 1(c).[17,24] Although there are strong intensity modulations because of the photoemission matrix element effect, they are established to disperse parabolically as indicated by broken lines. The $m3$ band crosses Fermi energy (E_F) almost exactly at the $\times2$ boundary ($\mathrm{ZB}_{\times2}$ in the figure) of the surface Brillouin zone and has a minimal dispersion in the interwire direction [Fig. 1(b)]. That is, the FS of $m3$ is relatively well nested with a half electron filling and was naturally related to the instability of the metallic phase and the $\times2$ PLD.[17,24] Below T_c, it is simply folded back at $\mathrm{ZB}_{\times2}$ to open an energy gap at E_F as expected in the CDW picture. On the other hand, $m1$ and $m2$ with smaller electron fillings exhibit a more complicated behavior to change into a single gapped band below T_c making the surface fully insulating.[24,27] These band structures above and below T_c were fully reproduced in density-functional-theory calculations based on the 4×1 undistorted structure[21] and the 8×2 hexagon-type distortion, respectively.[22] The latter tells us that the unexpected behavior of $m1$ and $m2$ stems from the complexity of the atomic structure (the "internal degree of freedom") of the wires due to the shear distortion between the two zigzag In chains within a single wire.

The above band structure is modified systematically by the adsorption of a tiny amount of Na atoms. Figure 1(d) shows an ARPES intensity map for the surface with 0.007 ML of Na at 300 K. The triple metallic bands are shifted to higher binding energy while keeping their dispersions and metallic nature. That is, the electrons are doped to the wires. The doping can be further illustrated by the momentum distribution curves at E_F [Fig. 1(e)] that clearly show the monotonic expansion of the electron pockets. The amount of electrons within each band can be determined from the Fermi wave vectors (the area of the Fermi surfaces) as a function of the Na coverage [Fig. 1(f)]. This indicates that roughly a single electron is donated to the surface from each Na adsorbate atom.

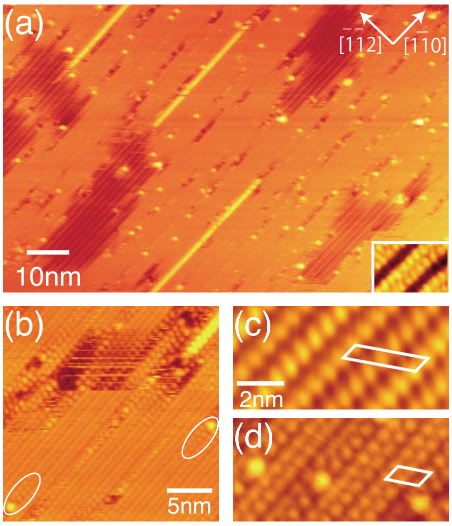

FIG. 2. (Color online) (a) An empty-state STM image of the In/Si(111) surface with 0.002 ML of Na at 110 K taken at the sample bias (tunneling current) of 0.3 V (20 pA). The inset shows the close-up image of the 4×1 domain (−0.3 V). (b) An enlarged images of the same surface showing the phase fluctuation. The circled areas exhibit the local $\times2$ distortions induced by Na adsorbates (bright protrusions). Closeups of the (c) 8×2 and (d) Na-induced 4×2 parts in the filled state (−1.0 V) taken at 77 K. The corresponding local unit cells are depicted.

On the pristine surface, the 4×1 phase [Fig. 2(a) inset] transits into the 8×2 structure [Fig. 2(c)] rather abruptly below T_c. The areal fraction of the two phases are plotted in Fig. 3(a) as a function of temperature, where the 8×2 domain covers more than 90% of the whole surface at 110 K. The doped electrons greatly and globally affect the surface below T_c. Figure 2(a) shows an STM image of the surface at 110 K with a very small amount of Na (~0.002 ML) deposited. The 8×2 domains [dark ones in Fig. 2(a)] shrink down to below 25% and the bright domains dominate after the doping. The structure of the bright domain itself is largely the same as the 4×1 phase above T_c. Even at 110 K, the 8×2 domain is not stable at all but fluctuating as shown in Fig. 2(b). A similar phase fluctuation was observed on the undoped surface but only close to the T_c of 125 K.[25] At a lower temperature of 77 K, as shown in Fig. 4(a), the surface changes mostly into the 8×2 phase but the small areas around adsorbates exhibit a distorted structure, a 4×2 structure as discussed in detail below.

The areal fraction for the doped surface as shown in Fig. 3(a) clearly indicates that the $4\times1\rightarrow8\times2$ transition is substantially suppressed. The bright domains noticeably contain prominent protrusions and lines. The protrusions are assigned as mostly single Na adsorbates based on their density. This confirms that the suppression of the transition is triggered by the Na adsorption. Some of the adsorbates are mobile on the surface and the bright lines are thought to be the

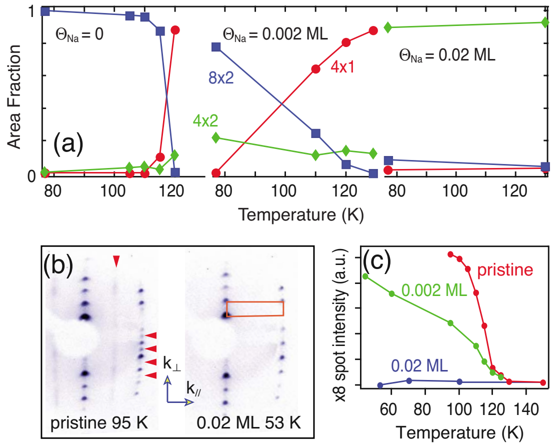

FIG. 3. (Color online) Evidences for the suppression of the phase transition on Na-deposited Si(111)4 × 1-In surfaces. (a) and (c) show temperature dependence of the area fraction of 4 × 1, 8 × 2, and 4 × 2 phases, and the intensity of the ×8 spot in LEED, respectively, for the pristine and Na-deposited Si(111)4 × 1-In surfaces. As shown in (b), LEED shows the 4 × 1 periodicity represented by the rectangle down to 53 K for the highly doped surfaces. The ×8 spots and ×2 streak, which are indicated by the arrowheads in (b), appear on the pristine surface below 120 K.

traces of the adsorbates diffusing along the wires (as probably pushed or pulled by the STM tip). Supporting this assignment, the lines appear and disappear suddenly at 110 K and are rarely observed at a lower temperature of 77 K.

The above temperature dependence is corroborated by low-energy-electron diffraction (LEED). The intensity of the 8 × 2 feature in LEED becomes substantially weaker below T_c on the doped surfaces [Fig. 3(c)] as the transition is suppressed. The surface, when it was heavily doped ($\Theta_{\mathrm{Na}} \sim 0.02$ ML), showed the 4 × 1 LEED pattern even at 50 K [Fig. 3(b)]. The above results clearly demonstrate that *the systematic electron doping into atomic wires is enabled simply by the alkali-metal deposition and the doping drastically changes the global property of the wires below* T_c.

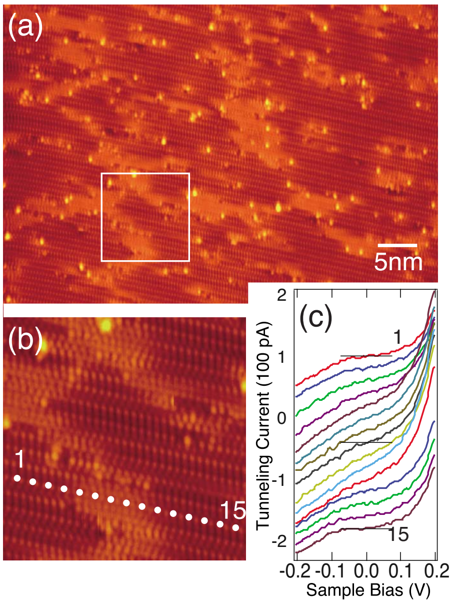

FIG. 4. (Color online) (a) The same surface as in Figs. 2(a) and 2(b) taken at 77 K and 0.5 V (60 pA). (b) enlarges the area enclosed with the square in (a). (c) STS *I-V* curves taken on the points 1–15 in (b). Horizontal lines are put on several curves to feature the slope at the zero bias.

As clearly shown in Fig. 2(a), the change in the surface by the very low-density Na adsorbates is nonlocal. It would thus be natural to attribute the suppression of the transition to the *nonlocal* change in the electron filling as manifested by the measured band dispersion (Fig. 1). This clearly evidences that the 4 × 1 → 8 × 2 transition is at least partly driven electronically. A previous STM and reflection-high-energy electron diffraction study showed that a tiny amount of In changes the 8 × 2 phase into the 4 × 1 structure below the transition temperature, while its mechanism was veiled.[31] Our finding is consistent with the very recent experiment where the same transition could be controlled by the photoinduced charge carriers; the photoinduced charge carriers change the surface-band bending, which, in turn, affect the electron filling of the metallic surface state.[32] On one hand, in the simple CDW picture, the transition is readily understood to be suppressed due to deterioration of the commensurate nesting of the *m*3 band. The deviation from the exact nesting condition would prevent the transition or lower the transition temperature as shown in the present experiment. The latter can readily occur when there exists a substantial commensurate interaction between the lattice and charge modulation.[33] Note, however, that the present result does not directly indicates the exclusive role of the *m*3 band since the doping changes the electron filling of all three bands. A more complicated electronic mechanism can be possible through interband interactions.[24] On the other hand, theoretical studies suggested that the transition is not a CDW type but driven simply by freezing the thermal lattice fluctuation, where the 4 × 1 structure is thought to be the thermally fluctuating and thus disordered 8 × 2 structure.[21,22] In this picture, it seems not clear how the very small increase in the electron filling and the very low coverage adsorbates can change drastically the transition temperature, that is, the lattice dynamics, of the whole surface.

Beyond the global change in the surface by the doping, we already mentioned that each Na adsorbate induces a local ×2 modulation along the wire, which extends typically to 2–8 nm [Fig. 2(b)]. This structure has two rather symmetric rows of ×2-period protrusions as shown in Figs. 2(b) and 2(d), which are in clear contrast to the well-known STM image characteristics of the 8 × 2 phase [Figs. 2(c)]. Similar local 4 × 2 structures were reported previously even at room temperature around a Na adsorbate[34] as well as H and O impurities[35] and vacancy-type defects [see Fig. 2(b)].[25] The modulation is the strongest around the adsorbates and decays as going away from them. In spite of the modulation in real space, the ×2 feature is not reflected in the LEED pattern because of the lack of a long-range lateral coherence of the modulation. The distinction between the Na-induced 4 × 2 and the pristine 8 × 2 phase is manifested further from the observation that some parts of the surface fluctuate between these two phases as shown in Figs. 5(a) and 5(b). The Na-

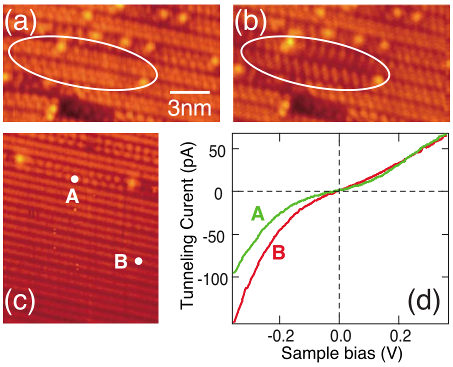

FIG. 5. (Color online) (a), (b) Successive STM images (with a 25 min interval) showing the phase fluctuation (within the ellipse) on the In/Si(111) surface with 0.05 ML of Na at 77 K. The tunneling condition was −0.3 V (70 pA). (c) An STM image (0.3 V, 50 pA) of the surface with 0.002 ML Na at 130 K and (d) STS *I-V* curves taken on the Na-induced $4\times 2(A)$ and pristine $4\times 1(B)$ parts.

induced 4×2 structure shows only a marginal temperature dependence; it survives around Na even at well below T_c [Fig. 4(a)].

The 8×2 and 4×2 phases are also contrasted in their electronic structure. Figure 4(c) shows scanning tunneling spectroscopy (STS) *I-V* curves taken along the linear trace in Fig. 4(b), which passes through the 4×2 phase surrounded by the 8×2 phase. The *I-V* curves show a significant slope at E_F on the 4×2 phase. That is, the 4×2-Na structure is metallic although it has a $\times 2$ PLD along the wires. However, as shown in Figs. 5(c) and 5(d), the metallic density of states (DOS) at E_F, i.e., the slope at the zero bias, on the well-developed 4×2 structure is apparently reduced from that of the undistorted 4×1 structure. This reminds us of the theoretical study which suggested a stable 4×2 configuration with a metallic band structure but with a reduced DOS at E_F.[23] We note that the STM image simulated for this model, based on the dimerization of the outer row In atoms within each wire, is very similar to the observed ones for Na-induced 4×2. Another previous theoretical study reported that a similar dimerization is readily formed by H adsorbates.[35] We thus suggest that the present local 4×2 structure also has a similar dimerized structure.

The present finding reveals the distinct global and local actions of the dopant atoms and suggests that the electronic and structural role of the adsorbates are rather decoupled. The electron doping is obviously nonlocal to suppress the transition globally while the structural distortion is fairly short ranged to yield a different local phase with even a distinct electronic state. The length scale of the 4×2 distortion is about 5 nm at 110 K for a single isolated Na adsorbate, which roughly coincides with the average size of the 4×2 domains left at 77 K. On the other hand, a recent STM study showed that during the phase transition a minor part of the surface exhibits a distinct 4×1 *undistorted* structure but with a reduced DOS at E_F.[36] This report shares with the present observation the point that the lattice and electronic degrees of freedom can be separated in the present system, at least in a rather short length scale. The control of the metal-insulator transition by dopants or charge carriers[32] would be important in utilizing the atomic wire arrays in more realistic device structures.

This work was supported by KOSEF through the Center for Atomic Wires and Layers of the CRi program.

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