Instability and Charge Density Wave of Metallic Quantum Chains on a Silicon Surface

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Self-assembled indium linear chains on the Si(111) surface are found to exhibit instability of the metallic phase and 1D charge density wave (CDW). The room-temperature metallic phase of these chains undergoes a temperature-induced, reversible transition into a semiconducting phase. The 1D CDW along the chains is observed directly in real space by scanning tunneling microscopy at low temperature. The Fermi contours of the metallic phase measured by angle-resolved photoemission exhibit a perfect nesting predicting precisely the CDW periodicity. [S0031-9007(99)09330-8]

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Among the exotic physical phenomena of low-dimensional materials, of particular recent interest, are quasi-one-dimensional (quasi-1D) metals which often exhibit Peierls-like instabilities and are proposed also to exhibit unusual non-Fermi liquid ground states [1–5]. In such metals, electrons and holes near the Fermi level often couple strongly with a lattice vibration, thereby resulting in a periodic spatial modulation of charge—a charge density wave (CDW) and an electron band gap at the Fermi level—the CDW gap [3]. So far, only a very limited number of material systems, such as organic conductors [6], Pt chain compounds [7], transition metal trichalcogenides [8], and transition metal bronzes [9] have been shown to exhibit the Peierls instability, which are all based on 3D materials with strong anisotropy in their electronic band structures.

Here we introduce another, completely new, 1D metallic system composed of self-assembled atomic chains on a 2D solid surface, in particular, In chains on the Si(111) surface [the Si(111)-(4 × 1)-In surface [10–16]]. We find that this system exhibits a temperature-induced, reversible transition in which a large fraction of the density of electron states at the Fermi level is extinguished by gap formation. The periodic lattice distortion (PLD) was revealed by diffraction and, moreover, the 1D CDW along the chains was observed directly with striking clarity in real space by scanning tunneling microscopy (STM). The Fermi contours of the room-temperature metallic phase exhibit a perfect nesting, which precisely predict the periodicity of the CDW/PLD observed at low temperature.

The experiments were done in three difference locations using various surface-structure and electronic-structure probes. (i) The spatial charge distributions and structures of surface In chains were probed by temperature-dependent STM and reflection high-energy electron diffraction (RHEED). (ii) Angle-resolved photoemission (ARP) was employed to study the surface electronic band structures and their temperature dependence. (iii) Finally, the Fermi contours, of crucial importance for the CDW systems [3], were determined by measuring the momentum-resolved photoelectron intensity at Fermi level using ultrabright synchrotron radiation [17]. The Si(111)-(4 × 1)-In surface was prepared by *in situ* deposition of In with an effusion cell on to the well-ordered Si(111) surface: by a dose of ~0.9–1.2 monolayers of In at room temperature followed by annealing at ~570–670 K [10–16]. A vicinal Si wafer with 2° miscut from the (111) axis was used to grow single domain 4 × 1 [16] for the clarity in ARP experiments.

The RHEED pattern of the room-temperature Si(111)-(4 × 1)-In surface is shown in Fig. 1(a) with a 4 × 1 unit cell marked. This surface is known to consist of linear chains along the "×1" direction, which appear as bright stripes spaced 13.3 Å apart in the real space images obtained by STM [Fig. 2(a)] [11,12]. Although the atomic

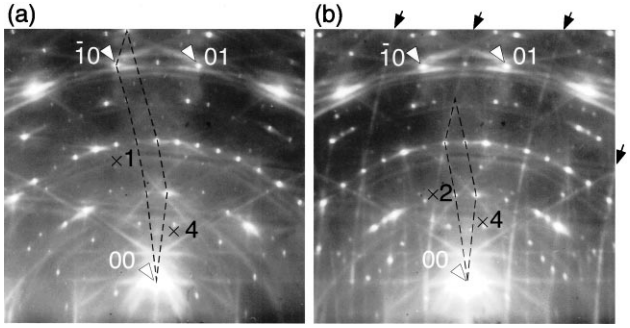

FIG. 1. Reflection high-energy electron diffraction (RHEED) patterns for (a) the room-temperature 4 × 1 phase and (b) the 4 × "2" phase at ~100 K. The 4 × 1 and 4 × 2 unit cells are depicted by dashed lines, and the streaks due to the periodicity doubling (×2) along the linear chain direction at ~100 K are indicated by the arrows.

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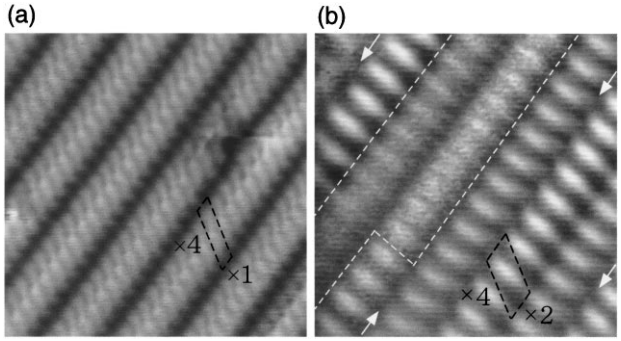

FIG. 2. Scanning tunneling microscopy images of (a) the room-temperature 4×1 phase and (b) the low-temperature ($\sim$65 K) $4 \times$ "2" phase were taken at the same sample bias voltage of -1 V (filled state) in the constant-height mode. The 4×1 and 4×2 unit cells are indicated by black dashed lines. The area of the characteristic fluctuating-charge density region (white dashed lines) and the phase mismatching between the neighboring chains (arrows) are observed.

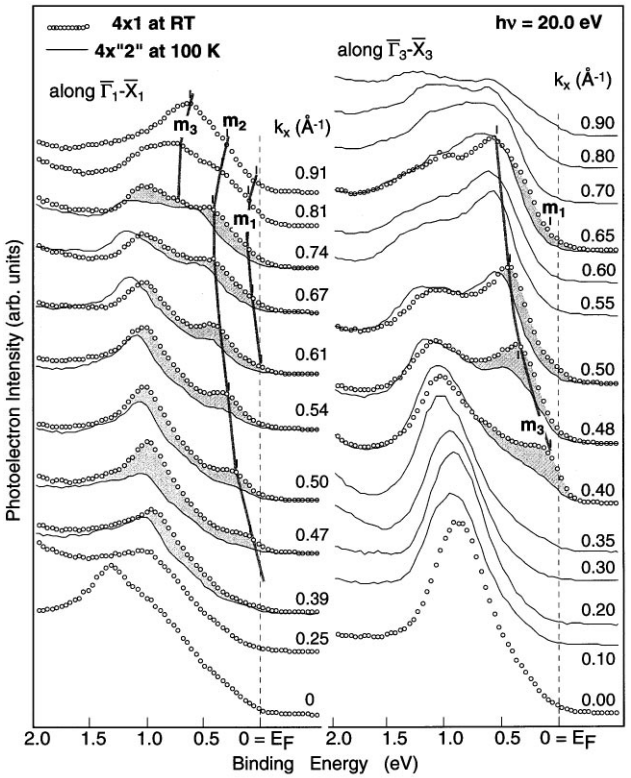

FIG. 3. Angle-resolved photoemission spectra for the room-temperature 4×1 phase (open circles) and the low-temperature ($\sim$100 K) $4 \times$ "2" phase (solid lines). The spectra are taken along the linear chain direction, that is along $\bar{\Gamma}$-$\bar{X}$ in the first (left) and the third (right) surface Brillouin zone ($\bar{\Gamma}$ at $k_x = 0$ Å^{-1} and $\bar{X}$ at $k_x = 0.82$ Å^{-1}). At $\sim$100 K, the reduction of spectral weights of the metallic states near Fermi level is evident as indicated by the hatching.

arrangement of the (4×1)-In surface remains under debate, bright features across the chains in the STM image are thought to represent multiple, closely packed In atomic rows [12–14]. The electronic structure of the (4×1)-In surface was previously studied by both angle-resolved inverse [15] and direct photoemission [16]. Those studies clearly showed that the (4×1)-In surface is metallic with three partially filled electronic bands. Furthermore, this triplet of metallic bands exhibits substantial 1D character since (i) they are surface electronic states localized on the topmost layers, and (ii) they cross the Fermi level with parabolic dispersions along only the linear chains but have rather flat sinusoidal dispersions perpendicular to the chains [16]. These bands are thought to originate mainly from In $5p_{xy}$ orbitals oriented parallel to the surface [16]. We have reconfirmed these results by measuring ARP spectra of the (4×1)-In surface as shown in Fig. 3. Three metallic bands, labeled $\mathbf{m}_1$, $\mathbf{m}_2$, and $\mathbf{m}_3$, were observed to disperse towards and cross the Fermi level. In particular, the Fermi cutoff due to the $\mathbf{m}_3$ band is obvious at $k_x \sim 0.4$ Å^{-1} along $\bar{\Gamma}_3$-$\bar{X}_3$. The $\mathbf{m}_2$ band appears strongest along the first Brillouin zone while $\mathbf{m}_3$ appears strongest along the third Brillouin zone. At the particular photon energy and k points shown in Fig. 3, the highest occupied surface state $\mathbf{m}_1$ is very weak.

The Fermi contours of these metallic surface states are determined experimentally as shown in Figs. 4(a) and 4(b) by measuring momentum-resolved photoelectron intensity in a narrow energy band (0.4 eV in full width) centered at the Fermi level as a function of the 2D electron wave vector (k) [17]. The Fermi contours are composed of straight or wavy lines in the (4×1) surface Brillouin zone. Their degree of straightness provides a direct measure of the 1D character or anisotropy of each band, since dispersion normal to the direction implies two dimensionality and also curved contours. The contours for $\mathbf{m}_1$ and $\mathbf{m}_2$ are substantially curved, and indeed may even form a closed electron pocket for $\mathbf{m}_1$. By contrast, the contour for $\mathbf{m}_3$ is clearly not closed and, more importantly, is perfectly straight to within the accuracy of our measurement ($\sim$0.02 Å^{-1}), suggesting nearly ideal 1D metallic character. Most importantly, the Fermi contours of $\mathbf{m}_3$ precisely bisect the (4×1) Brillouin zone along the line, again to within the experimental accuracy. This was determined not only from the data in Fig. 4, which might be subject to systematic errors due to the finite energy window used, but also by extrapolating the measured dispersion curves of $\mathbf{m}_3$ over almost two complete surface Brillouin zones. Thus a charge density modulation coupled to a lattice vibration of wavelength $2a_0$ along the In chains could lead to a Peierls-like instability at a sufficiently low temperature [3]. That is, the electrons and holes of the $\mathbf{m}_3$ band near Fermi level can couple with a unique momentum transfer of $2k_F$ spanning the Fermi contours to result in a diverging electronic response function. In this case the Fermi contours are perfectly "nested" with a "nesting vector" of $2k_F = \pi/a_0$ ($a_0 = 3.84$ Å) which is indicated by the arrows in Fig. 4 [3].

The instability of the 4×1 metallic phase is indeed observed when the surface is cooled to a temperature

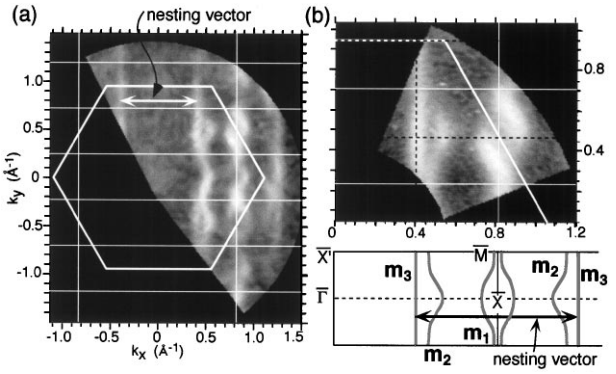

FIG. 4. (a) Fermi surface plot for the room-temperature 4×1 phase obtained by angle-resolved photoemission (at a photon energy of 85 eV) and (b) its details for an irreducible part of the surface Brillouin zone with a schematics of the Fermi contours determined. The 1×1 and 4×1 surface Brillouin zones are depicted with thick and thin solid lines, respectively. For clarity reasons, a rectangular 4×1 Brillouin zone is taken [15,16]. The obvious nesting vector for the CDW transition is indicated by arrows.

below ~100 K. The RHEED pattern at ~100 K shows streaks indicating a doubled periodicity along the chains, as pointed out by arrows in Fig. 1(b). These streaks indicate that there is a lattice distortion of a $2a_0$ periodicity along the linear chains, which is poorly correlated between chains. This is a characteristic feature of quasi-1D systems with minimal interchain interactions before they fall into 3D ground states [3]. The transition as observed in the temperature-dependent RHEED pattern is reversible. The low-temperature phase is labeled the ($4 \times$ "2")-In phase, where "2" indicates the presence of the streaks (not half-order spots) and distinguishes it from a well-ordered 2D 4×2 phase.

The surface electronic structure exhibits dramatic changes associated with the (4×1)-($4 \times$ "2") phase transition. The ARP spectra measured along the linear chains ($\bar{\Gamma}$-$\bar{X}$ in the 4×1 Brillouin zone) at room temperature and at ~100 K are compared in Fig. 3. The $4 \times$ "2" surface at ~100 K appears to be almost semiconducting without any electronic states crossing the Fermi level. Furthermore, the spectral features due to the Si bulk bands, not shown in Fig. 3, showed neither changes in intensity nor in binding energy. This reversible change reveals that the phase transition observed is coupled strongly with the electronic states near the Fermi level, which supports the Peierls-like instability in driving the transition. Because of the reduced intensity near the Fermi level and the limited energy resolution, the detailed band structure of the $4 \times$ "2" phase is not easily determined, although the size of Peierls half-band-gap is roughly estimated to be in the order of 50–100 meV.

Further, the charge density modulation induced by a Peierls instability can be observed directly by STM, which maps the local surface state densities [18–20]. The STM image of the ($4 \times$ "2")-In surface taken at ~65 K [Fig. 2(b)] shows a remarkable difference from that of the room-temperature 4×1 phase. The low-temperature STM images feature a pronounced $2a_0$-periodicity modulation of surface charge along the linear chains. The modulations are strikingly clear and simple over the complicated room-temperature STM image. Fourier transformation of this image produces $\times 2$ streaks, consistent with the corresponding diffraction patterns [Fig. 1(b)]. This is due to the frequent phase mismatching of the $\times 2$ modulation between the neighboring chains as indicated by the arrows in Fig. 2(b). This manifests the 1D nature of the charge density modulation observed.

It is now very clear that we have found a unique 1D CDW transition on solid surfaces, which is composed of "quantum wires" self-assembled on a 2D lattice. Although a 1D Peierls transition was proposed to explain a phase transition of Tl adsorbed on a Cu surface [21], the evidence for gap opening and CDW was ambiguous. Up to now, the real space observation of the CDW in quasi-1D materials was extremely limited to a very recent report on a bulk organic material with incommensurate CDW [18], although CDWs have been frequently imaged in 2D CDW systems [19,20]. We note that the STM imaging condition and the appearance of CDW phases of the present experiment are indeed very close to those of a bulk organic material [18]. However, due to the great advantage of a well-ordered surface system for STM imaging, the present observation has far more clarity and enables more detailed study of the spatial fluctuations of CDW, an essential aspect of 1D systems [3]. For example, we frequently observe pinning of the CDW phase by impurities or defects (not shown in Fig. 2). Another important fluctuation along the chains is observed in Fig. 2(b) as indicated by the white dashed lines: Two chains in the image have only very weak or possibly rapidly fluctuating charge density modulations. This 1D fluctuation in CDW, observed for the first time in real space, is attributed to a collective excitation such as phason or soliton [3]. Although detailed quantitative discussion of such fluctuations is beyond the scope of this Letter, the direct real space observation should provide a unique test case of the microscopic theories for CDW ground states, fluctuations, and excitations in 1D.

For the known bulk quasi-1D materials systems, finite interchain interactions ultimately produce 3D ground states. In the present case of a surface system, an evidence for finite 2D interchain coupling is observed. The STM images of the $4 \times$ "2" phase often show that the bright protrusions of $2a_0$ periodicity form a zigzag pattern across the chains with two chains as a unit. This gives rise to an $8a_0$ periodicity across the chains, which is barely observed in RHEED as very weak additional spots [Fig. 1(b)]. Although we observe both the $4 \times$ "2" and 8×2 phases at the temperatures measured here (~65 K for STM and ~100 K for RHEED), the true, low-temperature ground state is believed to be 8×2 with all adjoining CDWs locked in phase. The interchain interaction of the present system can be driven by the finite band dispersions of the

$\mathbf{m}_1$-$\mathbf{m}_3$ surface states perpendicular to the chains [16] or simply by the Coulomb repulsion of neighboring CDWs. Detailed studies over a wider temperature range are needed in order to understand the interactions involved in the 1D CDW and the 2D interchain ordering.

The lack of 3D interaction in the present system may result in more fundamental differences between the In chains and other bulk 1D materials through, most probably, the enhanced fluctuations. We note that the ratio of the estimated band gap to the transition temperature times the Boltzmann constant is ~ 10 and is thus much larger than simple mean field theory would predict [3]. This ratio is one of the largest among the known 1D CDW systems, although we acknowledge the need of higher-resolution quantification of the CDW gap. Fluctuations in 1D are known to suppress the phase transition temperature much lower than predicted by the simple mean field theory [22], which may explain the large band gap. Another surprising observation on the electronic structure is that the spectral intensities of all three metallic bands are significantly decreased near the Fermi level (the hatchings in Fig. 3) as the temperature is lowered while the Fermi contours in Fig. 4 implicate only $\mathbf{m}_3$ in driving the transition. The reason for this is not clear at this stage, although a similar observation was reported for a bulk CDW system [5]. Given these intriguing observations and the present debates on the anomalous spectral function of 1D materials, precise adherence to the very simple Peierls paradigm is not expected, and further detailed electronic structure investigation is required.

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