PHYSICAL REVIEW B **71**, 081310(R) (2005)

Electronic structure of one-dimensional indium chains on Si(111)

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(Received 5 January 2005; published 25 February 2005)

The driving force for the phase transition of quasi-one-dimensional (1D) indium chains on the Si(111)-4 $\times 1$ surface has been controversial. Using first-principles density-functional calculations we investigate the surface band structure of the low-temperature phase including a periodic lattice distortion. We find that the surface states m_2 and m_3 hybridize to yield a band-gap opening, while the surface state m_1 crosses the Fermi level. The simulated scanning tunneling microscopy (STM) images reproduce the features observed in the STM measurements, such as a double periodicity and an out-of-phase distribution in the filled- and empty-state images. The present results agree in many respects with recent photoelectron spectroscopy and STM experiments but do not support a 1D charge-density-wave mechanism accompanying a metal-insulator transition.

DOI: 10.1103/PhysRevB.71.081310 PACS number(s): 68.35.Bs, 68.35.Rh, 73.20.−r

Low-dimensional systems provide many interesting physical phenomena such as charge-density waves (CDWs), Jahn-Teller distortions, or the formation of non-Fermi-liquid ground states.[1] Recently, self-organized one-dimensional (1D) metallic chains on silicon surfaces have attracted much attention because of technological applications for the formation of atomic-scale structures.[2,3] As a consequence of a rapid development in lithography, the size of electronic devices is expected to be reduced down to the atomic limit where quasi-1D systems can be utilized as atomic-scale interconnects.

An important example of quasi-1D systems is the self-organized indium chains on the Si(111) surface.[3–11] Each 1D indium chain is composed of the two zigzag rows (see Fig. 1).[11] Using angle-resolved photoemission (ARP), scanning tunneling microscopy (STM), and reflection high-energy electron diffraction (RHEED), Yeom *et al.*[3] found that this system undergoes a reversible phase transition from a high-temperature 4×1 structure to a low-temperature $4\times$"2" structure at about 100 K. Here, "2" means the presence of half-order streaks (along the chain direction) rather than peaks in a RHEED pattern, indicating little correlation between the chains which contain a periodic lattice distortion. The ARP study[3] of Yeom *et al.* found a dramatic change in the surface-state bands (denoted as m_1, m_2, and m_3) between the 4×1 and $4\times$"2" structures, indicating that the former is metallic whereas the latter is almost semiconducting without any electronic states crossing the Fermi level. However, according to later low-temperature ARP data[7] of Yeom *et al.*, the two surface states m_2 and m_3 exhibited pseudolike band gaps with their remaining spectral weights at the Fermi level. Mainly from the presence of a half-filled metallic band (m_3) which has a nearly flat Fermi surface, Yeom *et al.*[3,7] interpreted the observed phase transition in terms of a 1D CDW mechanism or, equivalently, a Peierls instability along the indium chain. On the other hand, an x-ray diffraction (XRD) experiment[4] observed a low-temperature $8\times$"2" structure which is not fully developed even at 20 K, implying that the phase transition is not driven by a CDW. Moreover, our previous[5] first-principles density-functional calculations showed that both the 4×1 and 4×2 structures have three metallic bands crossing the Fermi level. Recently, other ARP, scanning tunneling spectroscopy (STS), and STM experiments of Yeom and his co-workers[8,9] obtained more information on the temperature-dependent electronic structures of the In/Si(111) system. This recent ARP experiment[8] observed that the three surface-state bands m_1, m_2, and m_3 clearly exhibit a band-gap opening below the transition temperature T_c, indicating a metal-insulator transition. The STS experiment[9] estimated this energy gap as $\sim$0.16 eV. Using a temperature-variable microscopic four-point probe method, Tanikawa *et al.*[10] found a dramatic change of electrical conductivity around 130 K and estimated an energy gap of $\sim$0.3 eV, which is two times larger than that estimated by the STS. It is noticeable that the recent STM experiment[9] also observed that at low temperatures below T_c the charge-density maxima (i.e., bright protrusions) in both the filled- and empty-state STM images not only doubled along the indium chain but were also completely out of phase with each other, thereby demonstrating occurrence of charge ordering in the low-temperature phase. Based on their ARP, STS, and STM data, Yeom and his co-workers[8,9] proposed a gap-opening mechanism in a multiband system where only

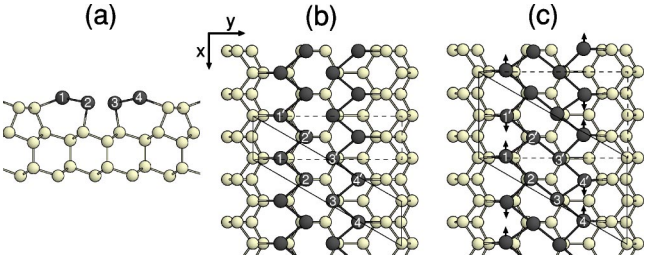

FIG. 1. Optimized structure of In/Si(111): (a) the side view of the 4×1 structure, (b) the top view of the 4×1 structure, and (c) the top view of the 4×2 structure. The dark and gray circles represent In and Si atoms, respectively. Two different choices for the 4×1 and 4×2 unit cells are indicated by the solid and dashed lines. The arrows in (c) show pairing patterns of the outer indium atoms. The **x** and **y** directions are $[\bar{1}10]$ and $[11\bar{2}]$, respectively.

one (m_3) band among the three surface bands has a Fermi-surface nesting with $2k_F=\pi/a_x$ (a_x is the lattice constant along the x direction: see Fig. 1).

In this paper, using first-principles density-functional calculations we reinvestigate the electronic structure of the In/Si(111) system within the 4×2 structure. We find that the m_2 and m_3 states hybridize to yield a band-gap opening. The size of this band gap is 0.19 (0.24) eV along the symmetry line ΓK ($K'X'$), in accordance with that ($\sim$0.16 eV) measured by a recent STS experiment.[9] However, the present calculations show that the m_1 state still crosses the Fermi level along the ΓK and $\Gamma X'$ symmetry lines. In addition, we find that the patterns of simulated STM images are strongly sensitive to the position of the Fermi level. If the Fermi level moves up toward the middle of the pseudogaps, the observed double periodicity and out-of-phase patterns in the filled- and empty-state STM images are well reproduced. Our results for the surface-state energy bands and the simulated STM images agree well with the recent ARP, STS, and STM experiments,[8,9] but are not compatible with a 1D CDW formation accompanying a metal-insulator transition.

Our first-principles calculations are performed using norm-conserving pseudopotentials[12] and the generized gradient approximation (GGA).[13] We used the same calculational parameters[14] as employed in our previous[5] calculations, except the number of **k** points for the **k**-space integrations. The present **k**-space integration was done with meshes of 224 (112) **k** points in the surface Brillouin zone (SBZ) of the 4×1 (4×2) unit cell, which is more than the 64 (32) **k** points used in our previous[5] calculations. Despite the present greater **k**-point samplings, there is little change in the atomic positions of the 4×1 and 4×2 structures, as well as in the energy difference between the two structures, compared with those of our previous calculations. The calculated surface band structure of In/Si(111)-4×2 is displayed in Fig. 2. Unlike our previous[5] surface band structure, where the m_2 and m_3 states cross each other along the ΓK and $K'X'$ symmetry lines just above the Fermi level, the present one shows that band gaps open along the the ΓK and $K'X'$ lines by 0.19 and 0.24 eV, respectively (see Fig. 2). In our previous calculations, the mapping of the surface bands was in error because of the choice of sparse meshes along the symmetry lines, but here we obtain the energy levels at dense meshes as shown in Figs. 2(b) and 2(c). Remarkably, the magnitudes of the present pseudogaps are close to the measured band gap ($\sim$0.16 eV) from the STS experiment.[9] However, as shown in Fig. 2(a), the m_1 state still crosses the Fermi level along the ΓK and $\Gamma X'$ symmetry lines, indicating that the 4×2 structure is metallic. Therefore, our band-structure calculations of In/Si(001)-4×2 do not support a metal-insulator transition claimed by Yeom and his co-workers.[3,7–9]

The formation of the pseudogaps in Figs. 2(b) and 2(c) is caused by the hybridization of the m_2 and m_3 states. Noting that the m_2 and m_3 states have similar charge distributions [see Fig. 2(c) in Ref. 5], such a hybridization easily takes place when the surface states around the X (M) point in the 4×1 SBZ are folded back around the Γ (X') point in the 4×2 SBZ [see the inset of Fig. 2(a)]. The band-gap opening in the 4×2 structure results in the energy lowering of the the

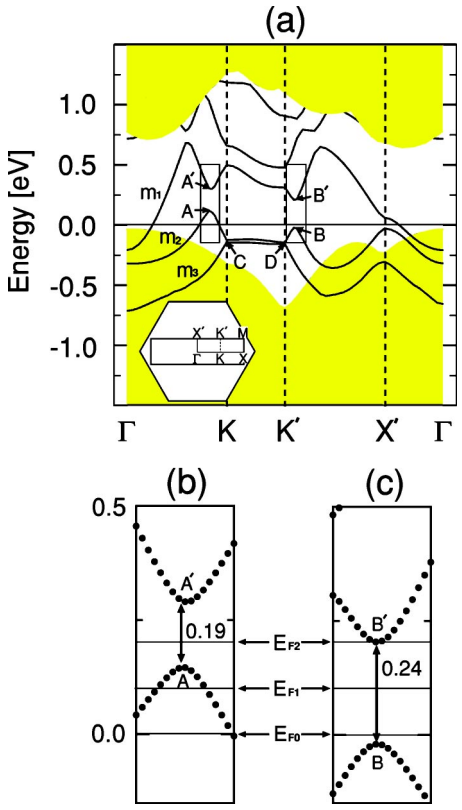

FIG. 2. Surface band structure of In/Si(111)-(4×2). The inset in (a) shows the surface Brillouin zone for the 4×1 and 4×2 unit cells with that for the 1×1 unit cell as a reference. The shaded areas are the projected bulk-band structure. (b) and (c) magnify the calculated energy levels around A, A', B, and B', equivalent to the two boxes in (a). Three different choices for the Fermi level (i.e., E_{F0}, E_{F1}, and E_{F2}) are given in (b) and (c): see the text.

m_2 and m_3 states near the K and K' points [i.e., at the points A and B in Fig. 2(a)], consistent with low-temperature ARP data[7] where the edges of the m_2 and m_3 states around the K point shift away from the Fermi level. Despite the significantly reduced spectral wights of the m_2 and m_3 states near the Fermi level, the ARP data of Ref. 7 showed some remaining spectral weights representing the *pseudogap* nature. It is notable that this low-temperature ARP data showed the presence of the m_1 state, though its intensity is very weak. In this sense, the earlier[7] ARP experiment finding the presence of m_1 near the Fermi level seems to differ somewhat from the recent[8] ARP experiment where the m_1 band disappears at low temperatures below T_c (see below).

Recently, Yeom and his co-workers performed another[8] ARP experiment to determine the dispersions of the surface states over more extended regions in the SBZ. At low temperatures they observed a clear gap opening of the m_2 and m_3 bands with the disappearance of the m_1 band. Here, the dispersions of the m_2 and m_3 bands along the XK (equivalently ΓK) and MK' (equivalently $X'K'$) lines are nearly parabolic with energy minima at the X point and around a half point between the M and K' points, respectively. In Ref. 8, it is difficult to find the energy minimum along the latter symmetry line because the intensity around the M point was very

weak. Such a parabolic feature of the m_2 and m_3 bands along the XK (or ΓK) and MK' (or $X'K'$) lines agrees well with our calculated surface-state bands [see Fig. 2(a)] of the 4 $\times 2$ structure. According to the ARP data of Ref. 8, the band-gap positions (i.e., energy maxima) of m_3 were found to be nearly at the K and K' points, while those of m_2 are somewhat shifted from the K and K' point. These experimental observations are consistent with our calculated band dispersion of Fig. 2, where the point C (D) corresponding to the maximum of m_3 along the ΓK ($X'K'$) line is at the K (K') point while the point A (B) corresponding to the maximum of m_2 is slightly shifted from the K (K') point. From their ARP data,[8] Yeom and his co-workers estimated that the maxima of m_2 and m_3 are located at 0.04 and 0.34 eV below the Fermi level, respectively. Here, the position of the experimental Fermi level does not correspond with our theoretical one, but the energy difference (0.30 eV) between the maxima of m_2 and m_3 is in good agreement with the present result (0.29 eV) between the A point [the maximum of m_2: see Fig. 2(a)] and the C point [the maximum of m_3: see Fig. 2(a)]. Also, the ARP data of Ref. 8 showed that the band-gap size of m_2 varies over the **k** space as much as 0.05 eV; that is, the band maximum along the XK line is higher than that along the MK' line. This behavior can be seen in our calculated dispersion of m_2 where the A point along the ΓK line is higher in energy than the B point along the $X'K'$ line by 0.16 eV. Thus, the overall dispersions of m_2 and m_3 agree well between the recent[8] ARP experiment and the present calculations. However, unlike the recent ARP experiment our calculations show no evidence for the disappearance of the m_1 band. Noting in the recent experiment that the spectrum intensity of the low-temperature phase was significantly reduced compared with that of the high-temperature phase, it seems that in the former phase the dispersion of the m_1 state could not be measured because of its weak intensity.

Using a combination of STM and STS, Park *et al.*[9] observed an energy gap opening of $\sim$0.16 eV as the temperature is lowered below T_c, and therefore claimed that the phase transition is truly a metal-insulator transition with a clear band gap rather than a pseudogap. According to their STM data for the low-temperature phase, the filled and empty state images showed the charge-density maxima with a double periodicty ($\times 2$) along the indium wires, and the maxima of the two images are completely out of phase with each other. Such a charge ordering together with a band-gap opening may be related with formation of a CDW in indium wires. However, our results for the band structure of In/Si(111)-4$\times$2 reveal that the m_1 state does not disappear but still crosses the Fermi level. This metallic feature of m_1 is not compatible with a simple 1D CDW mechanism for the phase transition. For comparison with the STM measurements, we simulate the STM images for the filled and empty states of In/Si(111)-4$\times$2. We have to notice that, because the STS experiment[9] measured a clear band gap at low temperatures below T_c, the position of the Fermi level (E_F) was not definitely determined within the band gap. Therefore, we choose the three different locations of the Fermi level to simulate the STM images: i.e., at (i) E_{F0} being the real Fermi level, (ii) E_{F1} located 0.10-eV above E_{F0}, and (iii) E_{F2} located just below B' [see Figs. 2(b) and 2(c)]. Our simulated STM images for the filled and empty states are displayed in Fig. 3. Here, the filled-state (empty-state) image mapping the electron density integrated at 0.3 eV downward (upward) from a given Fermi level is taken at about 3.8 Å above the outermost indium atom. (0.3 eV was the voltage at which the experimental STM data[9] was taken.) We find that the STM simulation [Figs. 3(a) and 3(b)] with a choice of $E_F=E_{F0}$ does not agree with the observed[9] STM images. On the other hand, with $E_F=E_{F1}$ and E_{F2} the filled- and empty-state images show bright spots with a double periodicity, which are completely out of phase with each other along the indium wires [see Figs. 3(c)–3(f). Especially, in case of $E_F=E_{F2}$ such double periodic and out-of-phase patterns are conspicuous, in good agreement with the experimental STM data.[9] It is interesting to note that the location of E_{F2} is 0.05-eV above the A point [i.e., the maximum of the m_2 band: see Fig. 2(b)], similar to the experimental[8] Fermi level which is located at 0.04 eV above the maximum of the m_2 band.

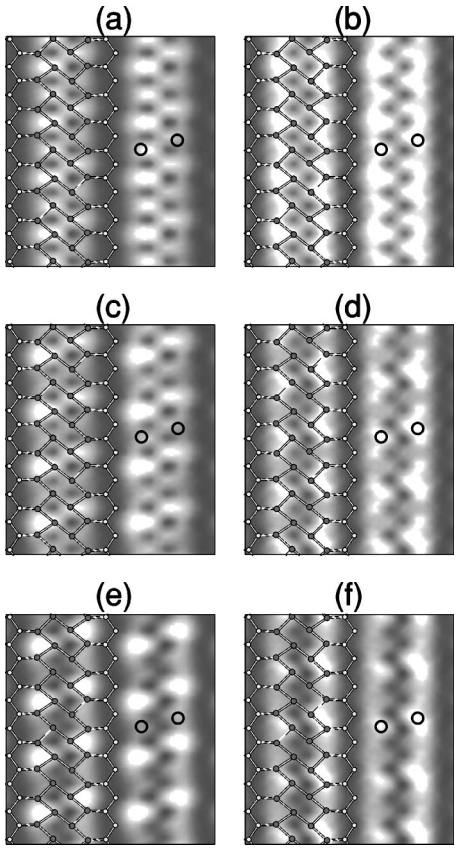

FIG. 3. Simulated STM images of In/Si(111)-(4$\times$2): (a) the filled-state image with $E_F=E_{F0}$, (b) the empty-state image with $E_F=E_{F0}$, (c) the filled-state image with $E_F=E_{F1}$, (d) the empty-state image with $E_F=E_{F1}$, (e) the filled-state image with $E_F=E_{F2}$, and (f) the empty-state image with $E_F=E_{F2}$. For the definition of E_{F0}, E_{F1}, and E_{F2}, see Fig. 2. The filled (empty)-state images are obtained by integrating the charge from E_F to $E_F-0.3$ (+0.3) eV. The images are taken at 3.8 Å above the outermost indium atom. The open circles mark bright spots in the empty-state images.

Since our band structure of In/Si(111)-4$\times$2 shows no evidence of being an insulator, the observed phase transition

is possibly due to an energy lowering lattice distortion with the hybridization of the surface states m_2 and m_3, rather than a simple 1D CDW mechanism.[3,7–9] In our previous[5] calculations, the m_2 state represents appreciable indium-p character localized between "inner" indium atoms [i.e., In_2, $In_{2'}$, In_3, and $In_{3'}$ in Fig. 1(c)], whereas the m_3 state originates mainly from the indium-Si interface bonding. Therefore, it is likely that the m_2-m_3 hybridization induces some attraction between In_2 ($In_{2'}$) and In_3 ($In_{3'}$) [see Figs. 1(b) and 1(c)]. As a result, the distances $d_{In_2-In_3}$ and $d_{In_{2'}-In_{3'}}$ become shorter, 3.06 Å, compared to 3.12 Å in the case of 4×1 structure. Because In_3 and $In_{3'}$ are on reflection planes of the 4×1 structure, a degenerate state would be obtained if we had chosen In_2 to be attracted to $In_{3'}$. Including the additional possibility of the pairing directions of "outer" indium atoms [i.e., In_1, $In_{1'}$, In_4, and $In_{4'}$ in Fig. 1(c)], each 4×2 unit cell has four degenerate configurations.[5] Thus, above T_c the atoms oscillate between their energy minima, their average positions yielding the 4×1 structure, whereas below T_c the atoms in each 4×2 cell are frozen randomly into one of the four degenerate ground states. This simple picture for the phase transition would provide an explanation for the RHEED (Ref. 3) and XRD (Ref. 4) observations that the low-temperature superstructure was not fully developed as $4\times$"2" (or $8\times$"2") reconstructions.

In summary, we reinvestigated the surface band structure of In/Si(111)-4×2 using first-principles density-functional theory calculations. Our results for the surface band structure showed that the 4×2 structure has a metallic feature, therefore not supporting a simple 1D CDW mechanism accompanying a metal-insulator transition. However, the dispersions of the surface bands m_2 and m_3 agree well with the recent ARP data.[8] The simulated scanning tunneling microscopy (STM) images also reproduce the features observed in the STM experiment,[9] such as a double periodicity and an out-of-phase distribution in the filled- and empty-state images. We hope future ARP experiments will observe the presence of the m_1 state crossing the Fermi level.

This work was supported by the KOSEF through the Quantum Photonic Science Research Center and the Welch Foundation (Houston, TX).

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[14] The surface is modeled by a periodic slab geometry. Each slab contains six Si atomic layers (not including the Si surface chain) plus an In overlayer, and the bottom Si layer is passivated by one H atom per Si atom. The thickness of the vacuum region between these slabs is about 10 Å. The electronic wave functions are expanded in a plane-wave basis set with a cutoff energy of 15 Ry.