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Nature of the broken-symmetry phase of the one-dimensional metallic In/Si(111) surface

H. W. Yeom,[1,*] K. Horikoshi,[2] H. M. Zhang,[3] K. Ono,[4] and R. I. G. Uhrberg[3]
[1]*Atomic-scale Surface Science Research Center and Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea*
[2]*Department of Physics, The University of Tokyo, Tokyo 113-0033, Japan*
[3]*Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden*
[4]*Department of Applied Chemistry, The University of Tokyo, Tokyo 113-0033, Japan*

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The phase transition of a metallic In chain structure on Si(111) was investigated by high-resolution photoemission. Core-level spectra clearly elucidate that the symmetry breaking at low temperature occurs only within the inner parts of the In chains. In the valence bands, the transition is accompanied by the formation of pseudogaps of 80–150 meV and the band backfolding with only marginal changes of the band dispersion. No sign of Luttinger liquid behavior is observed in the spectral function near the Fermi level. This result is generally consistent with the idea of a fluctuating one-dimensional charge-density wave state but conflicting with the present structure model for the low-temperature phase.

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Exotic electronic properties of one-dimensional (1D) electronic systems have attracted great interest, which include charge or spin density wave (CDW or SDW), triplet superconductivity, and Luttinger liquid (LL) behavior.[1] While most of the previous studies on 1D systems have been performed on limited types of anisotropic bulk materials,[1] very recently unique surface 1D metallic systems were identified on the flat and vicinal Si(111) surfaces with atomic-scale chain structures induced by In or Au adsorption.[2–4] These systems featuring nearly half-filled 1D electron bands bring about the possibility of detailed investigation of 1D physical properties in nanoscale and of atomic-scale fabrication of tailored 1D materials systems.

On the vicinal Si(557)-Au surface, the observation of spin-charge separation was reported,[3] which was denied from a subsequent study.[5] A Peierls band gap was introduced for an 1D surface state of Si(111)5×2-Au,[4] which was later discussed to be questionable.[4] The In induced 4×1 chain structure on Si(111) exhibits an ideal 1D Fermi surface and a unique *temperature-induced periodicity-doubling phase transition*.[2] This system was interpreted as an 1D CDW system driven by Peierls instability. Although the atomic structures of the Au-induced 1D chains are uncertain, that of 4×1-In was determined by a recent x-ray diffraction study.[6] The structure model was then confirmed by three independent *ab initio* calculations[7,8] in consistency with the available experiments.[2,6]

However, recently the nature of this phase transition was brought into question from two different points; (i) the 8×''2'' (or 4×''2'') low-temperature (LT) phase, as studied by x-ray diffraction, does not show any condensation into a well ordered 2D phase against the common wisdom of bulk quasi-1D systems[9] and (ii) the LT phase was shown to be not perfectly insulating.[10,11] In order to explain these intriguing properties, the ideas of simple total energy reduction due solely to the lattice relaxation[9] and of an exotic Fermi-to-Luttinger liquid transition[10] were introduced. Furthermore, a calculation[8] based on the recent structure model[9] of the LT phase denied the opening of the band gap at Fermi level in contradiction to the original experimental claim.[2] These recent results challenge the present understanding of the 1D metallic system and make it important to clarify the structural and electronic nature of the low-temperature phase further.

In the present Rapid Communication, we investigate in detail the valence-band and core-level photoemission from the RT 4×1 and LT 8×''2'' surfaces of In/Si(111). The questions to be answered are (i) how the periodicity doubling (or 1D CDW) is formed at LT, (ii) what are the band dispersions and the properties of the band gap (if any) at LT, and (iii) whether this system exhibits any non-Fermi-liquid behavior. Most parts of the present results are consistent with the *fluctuating Peierls transition* picture but with some complexities.

The photoemission experiments were performed at the angle-resolved photoemission beam line BL-33 of Max-I synchrotron radiation facility in Sweden.[12] The total energy resolution was set to 35 or 70 meV and ~60 meV in the valence band and core-level measurements, respectively. The angular resolution was only moderate to be set to 2° [~0.05 Å^{-1} for in-plane momentum ($k_\parallel$)]. The single-domain Si(111)4×1-In surface was prepared as reported before.[2] At 70 K, this surface exhibits the so called 8×''2'' (or 4×''2'') pattern with clear ×2 streaks and also with the 8× superspots,[2] which were thought to indicate the 1D CDW/PLD (periodic lattice distortion) along the chains and the extra interchain coupling,[8,9] respectively.[2]

The 4×1-In surface structure determined recently[6–8] has quadruple In atomic rows separated by Si zigzag chains (see the inset of Fig. 1). As shown in Fig. 1(a), the In $4d$ spectrum of this surface is composed of two well-resolved spin-orbit doublets (α and β) with an energy shift of 500 ±10 meV.[13] The spectral weight of α averaged over different photon energies and emission angles is 40–50% of the total In $4d$ intensity. This indicates two different In sites within each chain, which are populated with a ratio close to 1:1. The RT spectrum has notable asymmetry indicating metallic response of surface electrons in consistency with the presence of the metallic surface states. The asymmetry parameters (σ) in curve fitting exhibit a large difference be-

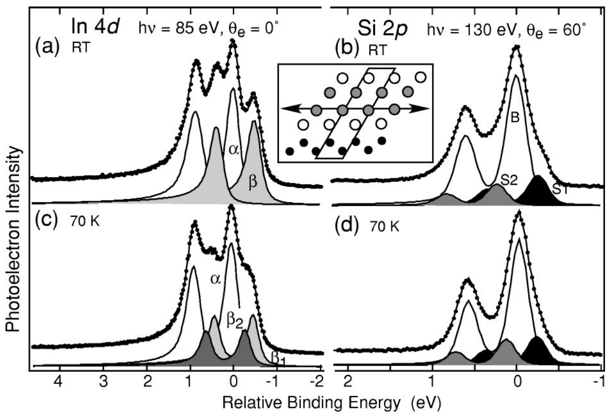

FIG. 1. In $4d$ (a), (c) and Si $2p$ (b), (d) spectra for the Si(111)4×1-In surface at room temperature (RT) and for the $8\times$''2'' (or $4\times$''2'') surface at 70 K. The inset shows the schematic representation of the topmost layer of the 4×1-In structure determined recently (Refs. 6–8), where the open, shaded, and filled circles represent the In atoms in the outer rows, In atoms in the inner rows, and Si chain atoms, respectively. In the inset, the arrow indicates the chain direction and the solid line the 4×1 unit cell.

tween α and β, 0.09 and 0.18, respectively. This suggests a very local difference of the metallic electron density between the two different In sites. The site represented by β has more metallic environment as also suggested by the smaller binding energy of β. Similar site-dependent electron screening was previously observed for 2D CDW systems.[14] Among the four In atomic rows in a chain, it is likely that the inner two rows have more metallic environment than the outer rows with direct in-plane bonding with Si. The α (β) sites can then be assigned to the In atoms of the outer (inner) two In rows of each chain (see the inset of Fig. 1). A recent theoretical calculation confirms this assignment and further reproduces the observed energy separation of α and β almost exactly.[8]

The Si $2p$ core levels at RT [Fig. 1(b)] also have asymmetry with $\sigma=0.035$ and feature two extra components ($S1$ and $S2$) in addition to the bulk contribution B [Fig. 1(b)], which are shifted from B by -0.27 ($S1$) and 0.24 eV ($S2$). At least the $S1$ component has surface origin, since its intensity is apparently suppressed at a more bulk-sensitive measurement. $S1$ is thus naturally attributed to the Si atoms of the zigzag chain on the topmost layer.

Upon cooling, core levels exhibit remarkable changes correlated with the phase transition. Most importantly, *the* β *component of* In $4d$ *splits into* β_1 *and* β_2 *with a splitting of* 0.20 eV *while* α *exhibits no dicernible change*. [Fig. 1(c)]. The *split-off* component β_2 is not evident in the raw spectra, but the line shape change, i.e., filling the valley between α and β of the RT spectrum, could not be accounted for otherwise. In addition, the asymmetry σ of β is reduced greatly from 0.17 to 0.11 although that of α does not change. In contrast to In $4d$, the changes of Si $2p$ are only *marginal*; slight change of the core level shifts from -0.27 to -0.23 eV and from 0.23 to 0.15 eV for $S1$ and $S2$, respectively, and a reduction of the asymmetric tail, from $\sigma=0.035$ to 0.01 [Fig. 1(d)]. The above spectral changes straightforwardly indicate that the phase transition induces only little change in the Si lattice but a significant perturbation to the In rows, especially, only to the inner In rows (the site β). That is, *the* PLD/CDW *along the chains is qualitatively confined on the more metallic inner* In *rows of each chain*. Such well-confined PLD/CDW might be related to the LT scanning tunneling microscope (STM) image showing a rather sharp charge-density maximum on the central part of a chain.[2,15]

The recent x-ray diffraction study reported that the PLD is comparable for both In (both inner and outer rows) and Si surface atoms within an order of ~0.5 Å.[9] This LT structure was not energetically favorable in a subsequent calculation, which instead suggested that the PLD of Si atoms is negligible while that of In rows amount to ~0.5 Å.[8] In this calculation the inner two In rows undergo an asymmetric distortion and the outer rows exhibit a symmetric dimerization. Thus the present core-level results seem to favor the structure suggested by the theory. However, even that theoretical model fails to reproduce the distinctive splitting of the β components observed: the theory expects the In $4d$ splitting due to the PLD of 50 and 80 meV for α and β, respectively. This discrepancy is not only quantitative but also qualitative since the experiment clearly shows the remarkable difference in the spectral changes of α and β. The limitation of the present LT structure models is even more serious when we consider the electronic structure as discussed below and the fact that the models could not reproduce the LT STM image observed.[8] We believe that the significant splitting of the In $4d$ β component is due to the charge ordering at LT. A similar size of CDW-induced core-level splitting was observed for the well-known 2D CDW systems.[14]

Figure 2 shows parts of an extensive series of angle-resolved photoemission spectra for the 4×1 and the $8\times$''2'' phases taken at a higher resolution than before[2] along the chain direction (along Γ_3-X_3). At RT three metallic surface states (m_1, m_2, and m_3) are clearly identified (see also Fig. 3).[2] The change upon cooling observed is consistent to the previous report: an overall suppression of spectral weight near Fermi level and the change of the apparent spectral shape extending up to 1 eV from Fermi level.[2] The spectra above 1.0 eV (data not shown) show perfect match between the RT and LT surfaces. No overall energy shift is observed between RT and LT in valence-band spectra, which is corroborated by core-level spectra with an accuracy of ±10 meV. The change near the Fermi level was previously interpreted as due to the Peierls gap opening but the LT band structure and the size/property of the gap was not clear.

Figure 3 shows the dispersions of the three metallic states at RT and 70 K. The overall band structures at RT and LT are essentially identical except for the region very close to Fermi level. The apparent change of spectra shown in Fig. 2 is thus thought to be not due to the formation of new bands at LT but to the change of the k-resolved photoemission matrix elements. Such matrix element changes, which redistribute the angle-resolved photoemission intensities, may be related to the change of the symmetry of surface state wave functions induced by the symmetry-breaking phase transition. However, near Fermi level, m_2 *and* m_3 *move clearly away from Fermi level without crossing it* as indicated by arrows in Figs. 2 and 3. Similar tendency is not confirmed for the m_1

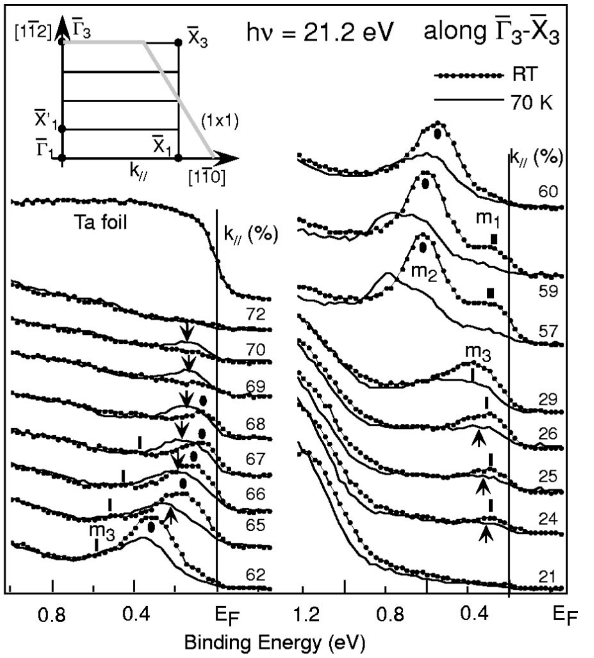

FIG. 2. Angle-resolved photoemission spectra taken with a photon energy ($h\nu$) of 21.2 eV for the RT 4×1 phase (dots and lines) and the 8×''2'' (or 4×''2'') surface at 70 K (solid lines). The spectra are taken along the linear chain direction, that is along $\overline{\Gamma}_3$-$\overline{X}_3$ in the surface Brillouin zone shown and the in-plane momentum ($k_{\parallel}$) along $\overline{\Gamma}_3$-$\overline{X}_3$ is specified in percentages of the full span of $\overline{\Gamma}$-$\overline{X}$-$\overline{\Gamma}$ (1.64 Å^{-1}). The spectrum of a Ta foil taken at RT is also shown.

due to its weak intensity. Those changes near Fermi level are consistent with the opening of the band gaps and the folding of the bands. The intensity of the folded bands is very weak and decaying as observed commonly for CDW related systems.[16]

The details of the gaps can further be elucidated by higher-resolution measurements at the RT Fermi-level crossings. Figure 4 shows the higher-resolution spectra at two such k points where m_2 and m_3 cross Fermi level. The leading edges of the m_2 and m_3 peaks shift away from Fermi level by 75 ± 20 and 40 ± 5 meV, respectively. Assuming a symmetric gap, the size of the gaps is estimated to be 150 ± 40 and 80 ± 10 meV for m_2 and m_3, respectively. What is interesting is that even at 70 K, the m_2 and m_3 states have remaining intensity at Fermi level, roughly half of that at RT, indicating the *pseudogap nature*. This is consistent not only with the *partial* reduction of the asymmetry of the core levels shown above but also with the *partial* reduction of the metallic tail of the electron energy loss spectra at LT.[11] The LT phase at least at 70 K is still not perfectly insulating although the density of states at Fermi level is significantly reduced. Contradictorily, the recent calculation based on the LT structure model does not indicate any band gap opening.[8]

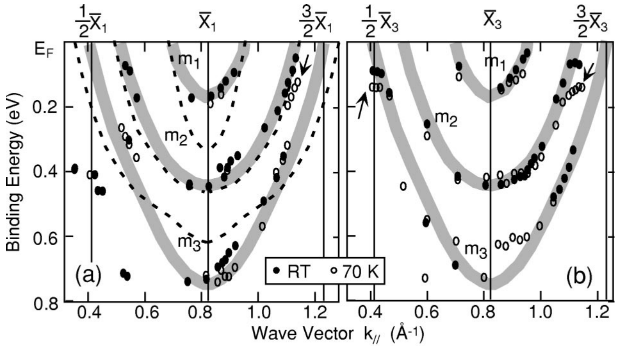

FIG. 3. The dispersion curves obtained from the angle-resolved photoemission spectra partly shown in Fig. 2 for the RT 4×1 phase (filled circles) and the 8×''2'' (or 4×''2'') surface at 70 K (open circles) along (a) the first ($\overline{\Gamma}_1$-$\overline{X}_1$) and (b) the third ($\overline{\Gamma}_3$-$\overline{X}_3$) SBZ lines. The thick gray lines are the eye guides for the experimental data and the dashed lines are calculated dispersions for the RT 4×1 surface[7].

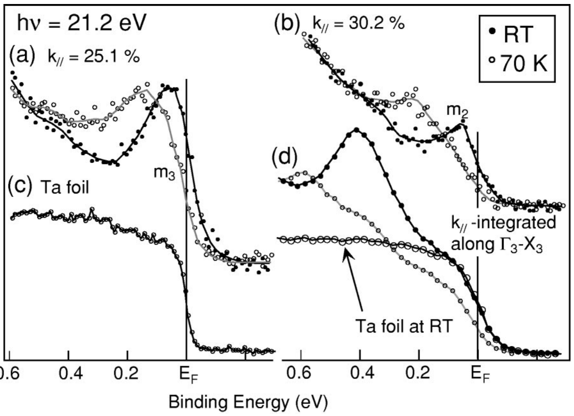

FIG. 4. High-resolution angle-resolved photoemission spectra taken with a photon energy ($h\nu$) of 21.2 eV for the RT 4×1 phase (dots and lines) and the 8×''2'' (or 4×''2'') surface at 70 K (open circles and lines) at the RT Fermi level crossings (a) m_3 and (b) m_2 bands, i.e., at $k_{\parallel}=25.1$ and 30.2%, respectively. (c) Similar spectrum for a Ta foil at 70 K. (d) Angle-integrated spectra at RT (dots and lines) and 70 K (open circles and lines) with a similar spectrum for Ta at RT superimposed.

The limitation of the LT structure models[8,9] in reproducing the In 4d core-level splitting, the STM images, and the band gap is in clear contrast to the success of the RT structure model in explaining most of the available experimental data.[6,7] The present discrepancy for the LT phase may be explained in two different ways: (i) the present structure model is far from the true LT structure or (ii) the present theory could not properly include the CDW of the LT phase. Considering the fact that the CDW would sensitively affect the In 4d core level, the STM image and the density of states at Fermi level, the latter explanation sounds plausible. Within the CDW idea, the remaining intensity at the Fermi level is understood in terms of (i) the intrinsic fluctuation of a 1D CDW system[17,18] or (ii) the pinning of the metallic domains by defects. Supporting the second idea, a recent STM study showed that a very low density of defects can drive the surface metallic locally or globally.[15] The extrinsic CDW fluctuation due to defects was also shown for a 2D system of Sn/Ge(111).[19] A recent photoemission study on 4×1-In also reported the formation of gaps for m_2 and m_3.[20] This study, however, gave quantitatively as well as qualitatively different information on the LT band structure, except for the existence of the band gaps themselves; (i) the whole band dispersions were shown to shift rigidly by 100–200 meV to high binding energy at LT, (ii) the leading edge shift associated with the gap opening were significantly bigger than the present ones, similar in size with the rigid shift, and (iii) the spectral shapes near Fermi energy at LT were ill defined with even certain structures *above* the leading edge.[20] These results are not consistent to the present and previous[2] photoemission studies and are in contradiction to the CDW idea even within the fluctuating CDW scheme introduced here. While any conclusive comment against this result is premature, we suspect that the rigid shift and the large band gap observed could be related to artifacts such as surface photovoltaic effects and surface contamination at LT.

The high-resolution data in Fig. 4 also exclude the possibility of LL behavior[10] for both RT and LT phase. This is because the quasiparticle of LL should have vanishing density of states at the Fermi level, which is obviously not the case in Figs. 4(a) and 4(b).[21] The possibility of LL behavior was also examined in the k-integrated density of states. The k-resolved spectra was integrated over a full span of a Surface Brillouin Zone (SBZ), separately for the first and the third SBZ. Such angle-integrated spectrum at RT matches perfectly with the Fermi edge spectra of a normal metal Ta. The LT angle-integrated (and also angle-resolved) data also show that it cannot be fitted with the power law lines with vanishing intensity at the Fermi level, which is a characteristic feature of LL.[21]

As presented above, most of the photoemission data are consistent to an 1D CDW phase transition with intrinsic or extrinsic fluctuations at LT along with the results of STM,[2,15] electron-energy loss spectroscopy,[11] and the surface conductivity measurement.[15] However, there still remain important questions to be studied. At first, it is not clear why both of the two metallic states show the gap opening although the exact nesting occurs only for m_3.[2,20] The present system may correspond to an 1D CDW system with two ‘‘competing’’ 1D metallic bands (m_2 and m_3).[20,22] Note that the Fermi-level crossings of m_2 and m_3 are very close.[2] The other issue is the nature and the role of the interchain interaction (as evident by the 8× order) in forming the LT ground state, which does not condense even at 20 K.[9] The interchain interaction is suggested to be quite weak and to occur in various forms by the recent theory[8] and indeed a recent STM study showed a variety of interchain couplings at 70 K.[15] The third issue is why the present system does not show the LL behavior irrespective of its ideal 1D electronic bands and Fermi surface as recently debated for bulk 1D system of $Li_{0.9}Mo_6O_{17}$.[23] Further study is highly requested for the above questions, which would definitely broaden our understanding of the low-dimensional electronic properties.

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*Corresponding author: FAX: +82-2-312-7090; Email address: yeom@phya.yonsei.ac.kr

[1] G. Grüner, *Density Waves in Solids* (Addison-Wesley, Reading, MA, 1994).

[2] H. W. Yeom *et al.*, Phys. Rev. Lett. **82**, 4898 (1999), and references therein.

[3] P. Segovia, D. Purdie, M. Hengsberger, and Y. Baer, Nature (London) **402**, 504 (1999).

[4] R. Losio, K. N. Altmann, and F. J. Himpsel, Phys. Rev. Lett. **85**, 808 (2000); K. N. Altmann *et al.*, Phys. Rev. B **64**, 035406 (2001).

[5] R. Losio *et al.*, Phys. Rev. Lett. **86**, 4632 (2001).

[6] O. Bunk *et al.*, Phys. Rev. B **59**, 12 228 (1999).

[7] R. H. Miwa and G. P. Srivastava, Surf. Sci. **473**, 123 (2001); J. Nakamura, S. Watanaabe, and M. Aono, Phys. Rev. B **63**, 193307 (2001).

[8] J.-H. Cho, D.-H. Oh, K. S. Kim, and L. Kleinman, Phys. Rev. B **64**, 233307 (2001). In fact, this work predicts a very small band gap for the m_3 state, but no gap for m_1 and m_2.

[9] C. Kumpf *et al.*, Phys. Rev. Lett. **85**, 4916 (2000).

[10] G. Le Lay *et al.* (unpublished).

[11] K. Sakamoto, H. Ashima, H. W. Yeom, and W. Uchida, Phys. Rev. B **62**, 9923 (2000).

[12] H. W. Yeom *et al.*, Phys. Rev. B **58**, 10 540 (1998).

[13] T. Abukawa *et al.*, J. Electron Spectrosc. Relat. Phenom. **80**, 233–236 (1996).

[14] H. P. Huges and J. A. Scarfe, Phys. Rev. Lett. **74**, 3069 (1995); J. Phys.: Condens. Matter **8**, 1457 (1996).

[15] S. V. Ryjkov, T. Nagao, V. G. Lifshits, and S. Hasegawa, Surf. Sci. **488**, 15 (2001).

[16] J. Schafer *et al.*, Phys. Rev. Lett. **83**, 2069 (1999); J. Voit *et al.*, Science **290**, 501 (2000).

[17] P. A. Lee, T. M. Rice, and P. W. Anderson, Phys. Rev. Lett. **31**, 462 (1973).

[18] R. H. Mckenzie, Phys. Rev. B **52**, 16 428 (1995).

[19] H. H. Weitering *et al.*, Science **285**, 2107 (1999).

[20] O. Gallus *et al.*, Eur. Phys. J. B **20**, 313 (2001).

[21] J. Voit, Phys. Rev. B **47**, 6740 (1993).

[22] C. Noguera, J. Phys. C **19**, 2161 (1986).

[23] J. D. Denlinger *et al.*, Phys. Rev. Lett. **82**, 2540 (1999); Jinyu Xue *et al.*, *ibid.* **83**, 1235 (1999).