Absence of dynamic fluctuation in metallic In chains on Si(111): Core-level and valence-band photoemission study

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We have studied in detail the evolution of the metal-insulator transition with temperature for the (4×1)-In chain structure on Si(111) using core-level and valence-band photoemission spectroscopy. Photoemission spectra unambiguously reveal that the high- and low-temperature phases are distinct with well-separated and characteristic spectral features. No sign of extra broadening or change of the spectral features was observed above the well-defined critical temperature. This result clearly rules out the existence of any dynamic fluctuation for the high-temperature metallic phase in contradiction with a recent theory [Phys. Rev. Lett. **96**, 136101 (2006)].

The interest in one-dimensional (1D) electronic structures continues to grow, fueled traditionally by exotic 1D phenomena, such as non-Fermi liquid state and Peierls instability, and more recently by the importance of nanowires in nano and molecular electronics.[1–9] Among various up-to-date 1D electronic systems, the self-assembled atomic wire arrays on Si surfaces have attracted particular attention due to the observation of temperature-induced metal-insulator transitions for In/Si(111),[4,5,8] Au/Si(553),[9,10] Au/Si(557),[11] and Au/Si(5512).[12] These transitions have been attributed to Peierls instability because of the partially filled 1D electronic bands and their nested Fermi surfaces with nesting vectors matching the periodic lattice distortions.[13–15] Various interesting physics issues were raised on these phase transitions such as the intriguing nature of the ground states at low temperature (LT) (Ref. 13) and the atomic-scale fluctuations near the transition temperatures (T_c's).[16–18]

However, the basic idea of Peierls instability in these systems was recently challenged by the contradicting theoretical interpretations based on dynamic structural fluctuations leading to order-disorder transitions for Au/Si(557) (Ref. 14) and In/Si(111).[15] No direct evidence of the fluctuating high-temperature phase is observed so far, calling for careful experimental tests. In particular, it is not trivial for such fluctuation scenarios to explain the temperature-induced change of electronic structures since they basically assume a thermally excited fluctuation between degenerate *insulating* ground states. Indeed, for the well-established examples of surface order-disorder transitions, such as the clean Si(001) and the Sn/Ge(111) surface, no change of electronic structures has been confirmed.[19,20]

In this work, we focus on the phase transition of In chains on Si(111) between the room-temperature (RT) 4×1 and the LT 8×2 phase.[4,5,13] For this system, the temperature-induced change of the electronic structure, in addition to the structural change, was confirmed through various methods such as angle-resolved photoemission spectroscopy,[4,5] scanning tunneling spectroscopy,[16,17] electron-energy-loss spectroscopy,[21] and transport measurements.[22,23] However, the previous density-functional-theory calculations could not reproduce the insulating band structure of the LT phase in clear

contrast to the impressive success for the atomic and band structures of the RT phase. Very recently, González, Flores, and Ortega introduced a structure model for the LT phase, which can reproduce the corresponding experimental band structure.[15] They further analyzed the thermal excitation from this model structure using molecular dynamics and explained the RT phase as a dynamically fluctuating one between the degenerated 8×2 LT structures.[15] The switching from one to another insulating 8×2 configuration passes through intermediate metallic configurations[15] and their increased occupation at high temperature was argued to account for the RT metallicity.

In order to verify this theoretical suggestion, we investigated the detailed temperature dependence of photoemission spectra through the (4×1)-(8×2) phase transition. The photoemission measurements have important merits in identifying the dynamical fluctuations[19,20] since (i) the time scale of the photoemission process is much faster (femtoseconds) than structural fluctuations (picoseconds) and (ii) both RT and LT phases of the present system have clear spectroscopic signatures in core levels and valence bands.[5,24] Indeed, González, Flores, and Ortega also expected that photoemission spectroscopy would show the evidence of the dynamical fluctuation as broadened or mixed-up spectral features at RT.[15] Our photoemission data, however, do not show any such broadening or mixture of the spectral features for any temperature above a well-defined T_c, for both core levels and band dispersions near Fermi level. This result supports a displacive-type phase transition between well-defined static RT and LT phases in accord with structural studies, transport measurements, and other spectroscopic results.[5,16,17,21–24]

The photoemission measurements for valence bands were performed using a high resolution angle-resolved electron analyzer (SES-100, Gamma Data) and He I radiation ($h\nu = 21.2$ eV).[9,11] The nominal energy and angular resolutions were better than 13 meV and 0.2°, respectively. In this system, extensive low-energy-electron diffraction (LEED) measurements were also performed. The In $4d$ spectra were measured with a photon energy of 102 eV on 8A1 undulator beam line of Pohang Accelerator Laboratory using a similar high-resolution electron analyzer (SES-2002).[25] The overall
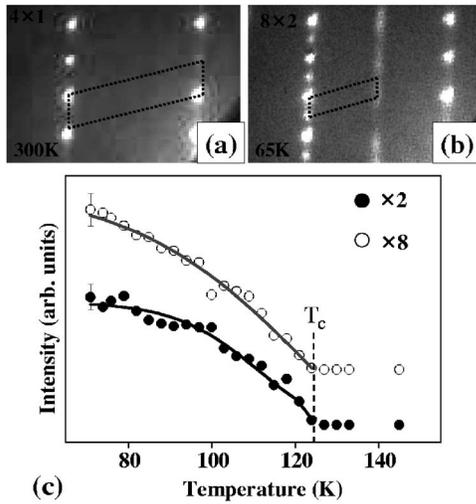
FIG. 1. LEED patterns of (a) the (4×1)-In (300 K) and (b) the (8×2)-In surface (65 K) at a beam energy of 82 eV. The corresponding unit cells are drawn by dotted lines. (c) The intensities of LEED spots for the transverse ($\times 8$) and longitudinal ($\times 2$) orders as functions of temperature. The T_c is uniquely defined as indicated by the dashed line. The error bars of the intensity measurements are also given and the solid lines are to guide to eyes.

FIG. 2. (a)–(c) Temperature-dependent energy band dispersions measured near the 4×1 Brillouin zone boundary ($\bar{K}$) of the In/Si(111) surface along the In wire direction ($\bar{\Gamma}$-$\bar{K}$, $[1\bar{1}0]$). The energy spectrum at $k_x = 2.65$ Å^{-1} [the dashed line in (a)] of each band map is attached, where the RT and LT bands are indicated by open and closed arrows, respectively. (d) Schematics of the RT (dashed lines) and LT (solid lines) band dispersions.

instrumental energy resolution was better than 40 meV. The temperature of a sample could be accurately controlled down to 40(75) K by a He (liquid N$_2$) cryostat and a feedback-controlled heater for valence-band (core-level) measurements.

The (4×1)-In structure is built up of In nanowires composed of four In atomic rows and separated by Si zigzag chains as determined by x-ray diffraction,[13] electron diffraction,[26] and theoretical calculations.[27] Note that this structure exists only instantaneously in the dynamical fluctuation scenario. Figure 1(a) shows the LEED pattern of the (4×1)-In surface at RT. The $\times 2$ LEED features are streaky at 125 K but become elongated spots at lower temperature further indicating the enhanced interwire coupling at LT. The $\times 2$ and $\times 8$ LEED spots appear abruptly from 125 K and their intensities increase rapidly up to ~ 90 K followed by slow increases below. This indicates that the $\times 2$ and $\times 8$ long-range orders occur almost simultaneously and the phase transits between ~ 90 and 125 K, as reported previously.[16] The increase of the diffraction intensities below ~ 90 K can be partly due to the decrease of the Debye oscillation. The simultaneous occurrence of the $\times 2$ and $\times 8$ long-range order was also confirmed by scanning tunneling microscopy (STM) measurement as the formation of 8×2 domains.[16,17] The 1D $\times 2$ fluctuation may precede the formation of 2D 8×2 domains but this precursory fluctuation does not have a sufficient long-range order to be detected in LEED.[16] For the temperature range of ~ 90–125 K, the STM measurements showed the coexistence of 8×2 and 4×1 domains. While the detailed transition dynamics deserve further study, it is clear that the transition has a well-defined T_c of 125 K and there is no trace of the LT phase above this T_c, at least as far as STM and LEED observe. In the dynamical fluctuation scenario, this well-defined T_c corresponds to the temperature
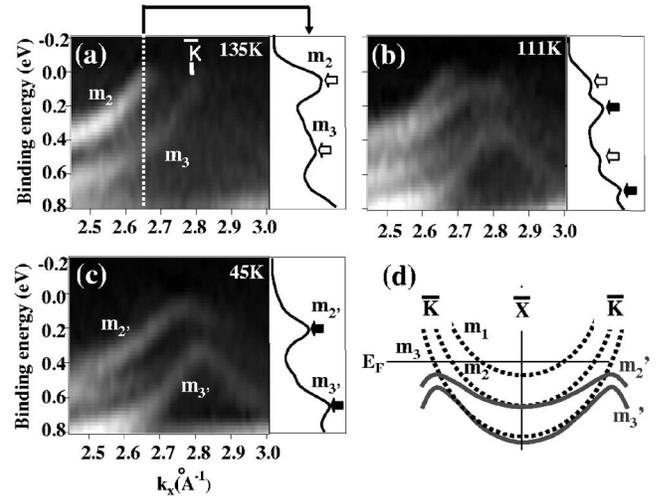
where the fluctuation between the 8×2 ground states becomes faster than the time scale of the STM and LEED measurements (longer than milliseconds).[15] Therefore, it is not obvious in LEED and STM whether the (4×1)-(8×2) phase transition is due to the dynamical fluctuation or not.

However, we can check the fluctuation with a femtosecond time scale through photoemission measurements. Figure 2 shows the temperature-dependent valence-band spectra of In/Si(111), where the energy bands near $\bar{K}$ (the Brillouin zone boundary) were measured along the wires. The energy bands of the 4×1 phase consist of three metallic ones with band fillings of 0.5 (m_3), 0.38 (m_2), and 0.11 (m_1).[5–7] The m_3 and m_2 bands are clearly shown in Fig. 2(a) to cross the Fermi level.[4,5] A recent experiment also unveiled the band dispersions of the 8×2 phase; the m_1 and m_2 bands are combined into a single insulating band (m_2') with an energy gap of 0.04 eV, while m_3 opens a larger energy gap of 0.34 eV resulting in another insulating band m_3' [Fig. 2(c)].[5] As is clear in the figures, the two sets of bands are distinct with different dispersions, especially near Fermi level, and are reproduced well in the theoretical calculations, although there is disagreement on the LT band structure between different theory groups.[27,28]

As mentioned above, the dynamical fluctuation scenario indicated that the electronic band structure above the apparent T_c should be a mixture of the bands of different configurations (insulating 8×2 and various instantaneous intermediate configurations with some metallic ones).[15] The weight of the metallic bands is then expected to grow gradually above T_c with the apparent broadening of spectral features at the expense of the spectral weight of the insulating bands as the temperature increases.[15] The spectral weight of LT bands would remain significantly by well above T_c.[29] In clear contradiction to this expectation, the band dispersions just above
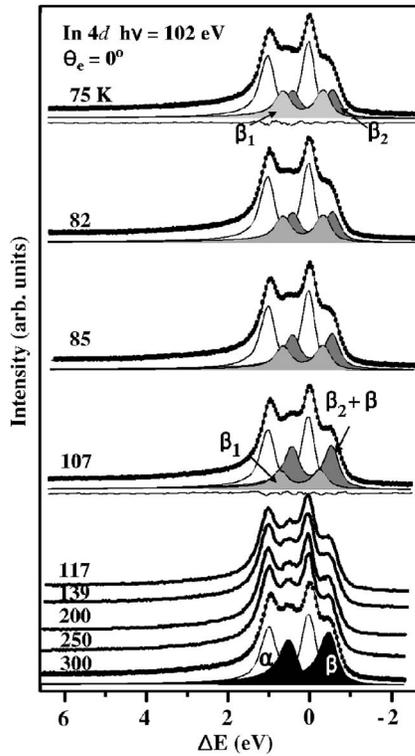
FIG. 3. Temperature-dependent In $4d$ photoemission spectra measured at the normal emission with a photon energy of 102 eV. The decompositions through standard least-squares curve fittings using asymmetric Doniach-Sunjic line shapes are given together. The fitted data (dots) are overlaid with the results of the fits (thin solid lines). Residues of the curve fits are also given for two representative spectra.

FIG. 4. Temperature-dependent intensities of β_1 (solid circles) and $\beta_2+\beta$ (β fully overlapped with β_2, open circles) components of In $4d$ spectra as determined by the curve fitting analysis. The intensities are given as the percentage of the total integrated intensity of each spectrum.

T_c [Fig. 2(a)] show only the well defined metallic bands of m_3 and m_2, which do not exhibit any further change up to RT except for the marginal broadening expected from the usual Debye lattice vibration. Note that the quantitative comparison of the widths of the spectral features is rather limited due to the change of their binding energies and symmetries. Only between ~90 and 125 K, the measurement exhibits a mixture of insulating and metallic bands as clearly shown in Fig. 2(b). Within this temperature window, two sets of bands transfer their spectral weights as expected from the growth of the insulating domains at a lower temperature. It is important that there is no trace of the insulating bands (m_2' and m_3') above T_c with little ambiguity; at $k_x=2.65$ Å^{-1} the splittings of the metallic RT and insulating LT bands are as large as 0.2 eV [Fig. 2(b)]. This conclusively denies the dynamical fluctuation scenario.

The absence of the dynamic fluctuation above T_c can also be shown in In $4d$ photoemission spectra, which reflect the instantaneous local charge distributions on In atoms. The In $4d$ spectrum at the bottom of Fig. 3 is for the 4×1 phase at RT. It is fitted well with two asymmetric components (α and β) with an energy shift of 0.50 eV as shown previously.[24] The asymmetric tails towards high binding energy indicate gapless excitations due to the metallic nature of In wires.[24] These components were previously interpreted to represent two different In sites, that is, the inner and outer In
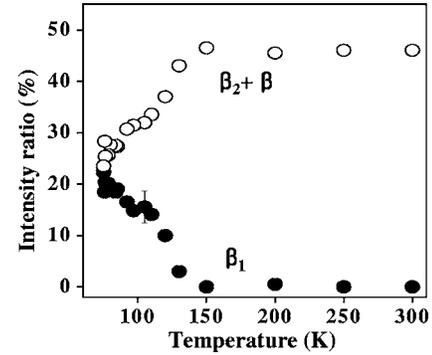
chains among the four within a unit wire.[24] The inner In chains are expected to have a larger metallic electron density to yield a lower In $4d$ binding energy (the β component).[24]

In contrast, for the LT phase (the top spectrum in the figure), one can notice an apparent line shape change of the β component with α intact. This change could only be reproduced by the decrease of β and the emergence of the spectral weight between α and β.[24] In the previous[24] and the present work, the extensive curve-fitting analyses based on various spectra taken at different photon energies, angles, and sample preparations consistently indicated that the β component splits into β_1 and β_2 with an energy splitting of 0.2 eV. In fact, the binding energies of β_2 and β are identical and, thus, cannot be distinguished. This characteristic splitting of β was previously interpreted as to represent the charge or lattice distortion on the inner In chains.[24] Irrespective of the interpretation of the In $4d$ changes, the spectroscopic signature of the LT phase is clear as β_1. With lowering temperature from RT, the In $4d$ line shape does not show any apparent change down to T_c but, only from T_c, the β component exhibits gradual change into β_2 and β_1 (Fig. 3). This trend can be quantified further as follows. Since β_2 and β are not separated, we treat the corresponding component at intermediate temperatures as $\beta_2+\beta$ and analyze the spectral change based on the decomposition into α, β_1, and $\beta_2+\beta$. The intensity change of the β_1 ($\beta_2+\beta$) component is extracted as summarized in Fig. 4. The intensity increase (decrease) of β_1 ($\beta_2+\beta$) is fully systematic and occurs only below T_c indicating again the increase of the 8×2 domains shown in STM and LEED. This tells clearly that the apparent phase change in LEED and STM measurements (with a slow time scale) is not different from the local lattice (or charge) modulations (up to a very fast time scale) and thus there is no dynamical lattice fluctuation above T_c. It should be noted further that the spectral linewidths of α and β do not exhibit any extra broadening between T_c and RT, except for the trivial thermal broadening of 30–40 meV as measured by the Gaussian widths of β and β_1, ruling out even any enhanced random fluctuation above T_c.

In conclusion, we measured the detailed temperature dependence of the valence-band and core-level photoemission

spectra of the Si(111)(4×1)-In surface in a wide temperature range through the (4×1)-(8×2) metal-insulator phase transition. We found that the spectral changes occur restrictedly from T_c of about 125 K down to ~90 K. No sign of the enhanced spectral broadening or the spectral features characteristic of the LT phase was observed above T_c. This result indicates clearly that there are no structural or electronic fluctuations above T_c within the time scale of photoemission process of femtoseconds ruling out the dynamic fluctuation mechanism of the phase transition.

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