

Metal-insulator transition on the Si(111)4 × 1-In surface with oxygen impurity

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We investigate with low-energy-electron diffraction (LEED) and angle-resolved photoelectron spectroscopy (ARPES) the effect of oxygen adsorbates on the phase transition of the Si(111)4 × 1-In surface. On this surface, oxygen was reported to increase the transition temperature (T_c) into the distorted 8 × 2 phase. We observed that while the T_c into the 8 × 2 phase increases up to 180 K, the substantial disorder is also induced on the surface. ARPES study reveals that the oxygen-induced 8 × 2 phase has the same insulating band structure with that on the pristine surface at a lower temperature. This indicates clearly that the oxygen-induced 4 × 1–8 × 2 transition is a consistent metal-insulator transition with that on the pristine surface. On the other hand, oxygen adsorbates slightly increase the band filling of the one-dimensional metallic bands of the 4 × 1-In surface. This contrasts with the expectation of the hole doping and the increased T_c , thus cannot be explained by the doping effect of adsorbates. A further study of the oxygen-induced 8 × 2 phase is requested to understand the microscopic mechanism of the adsorbate-induced elevation of the metal-insulator T_c .

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I. INTRODUCTION

Phase transitions of one-dimensional (1D) metallic systems formed along self-assembled atomic wires on silicon surfaces have attracted substantial interest during the last decade.^{1–6} The charge density wave (CDW) formation through metal-insulator transitions^{1,2,4,5} and, more recently, the 1D antiferromagnetic ordering was discussed.⁷ In particular, In atomic chains on Si(111) [referred to as the 4 × 1-In surface] has been the most extensively studied system with well defined multiple quasi-1D metallic bands and a clear symmetry-breaking metal-insulator transition into a 8 × 2 phase at about 130 K.^{1,3,8,9} The 8 × 2 insulating phase is thought to be a CDW state formed through a fairly complicated transition, where the structural, electronic, and phononic degrees of freedom interplay in an intriguing way.^{10,11}

Generally speaking, 1D electronic systems must be extremely susceptible to impurities and such impurity interactions have been a topic of extensive research. Indeed, there were a few interesting works also on impurity effects on the phase transition of the 4 × 1-In surface. Various adsorbates like In, Na, and H were reported to reduce the transition temperature (T_c) of the 4 × 1–8 × 2 phase transition, locally destabilizing the 8 × 2 phase.^{12–15} In contrast, an early study on Na adsorbates reported the increase of T_c up to room temperature (RT).¹⁶ Although the defects themselves were not characterized, the condensation of the 8 × 2 phase by native defects was also observed.^{3,17} However, a later scanning tunneling microscopy (STM) study showed that the local Na-induced phase is clearly different from the low temperature 8 × 2 CDW state and the CDW T_c itself is suppressed significantly.¹⁵ At a high Na coverage, the Na-induced local perturbations and the ordering of Na adsorbates themselves dominate.¹⁵ A Na adsorbate at a low coverage was shown to donate electrons into the 1D metallic state and the reduced T_c could largely be understood by the deviation from the

optimal doping.^{15,18} On the other hand, these works indicate that the influence of adsorbate impurities can be much more complex than the simple suppression of the CDW state since an impurity can in principle interact electronic, structural, and/or phononic degrees of freedom in different ways. In this respect, it is notable that one recent experiment suggested a significant and systematic increase of the 4 × 1–8 × 2 T_c by oxygen adsorbates.^{13,19} While the possibility of the hole doping by oxygen was introduced, the recent theoretical calculation indicated that both the electron and hole doping only reduce T_c .¹⁸ The nature of the interaction between oxygen and the 4 × 1-In surface, the electronic property of the oxygen-induced 8 × 2 phase, and the mechanism of the T_c increase are all unclear at present.

In order to understand the effect of oxygen on the metal-insulator transition of the Si(111)4 × 1-In surface, we performed temperature-dependent angle-resolved photoelectron spectroscopy (ARPES) experiments for various oxygen doses. We clarified that the oxygen-induced 8 × 2 phase has the same electronic band structure with the CDW phase of the pristine surface at low temperature. This verifies that oxygen adsorbates indeed increase the T_c of the metal-insulator transition. We also show that the oxygen adsorption increases the band filling of the 1D metallic bands in contrast to the expectation of the hole doping. It is inferred that the local bonding nature of oxygen adsorbates and the local strain induced would be important for the metal-insulator T_c increase.

II. EXPERIMENTAL METHODS AND STRUCTURE MODELS

ARPES experiments were performed in an ultra-high-vacuum chamber equipped with low-energy-electron-diffraction (LEED) optics. The base pressure was maintained

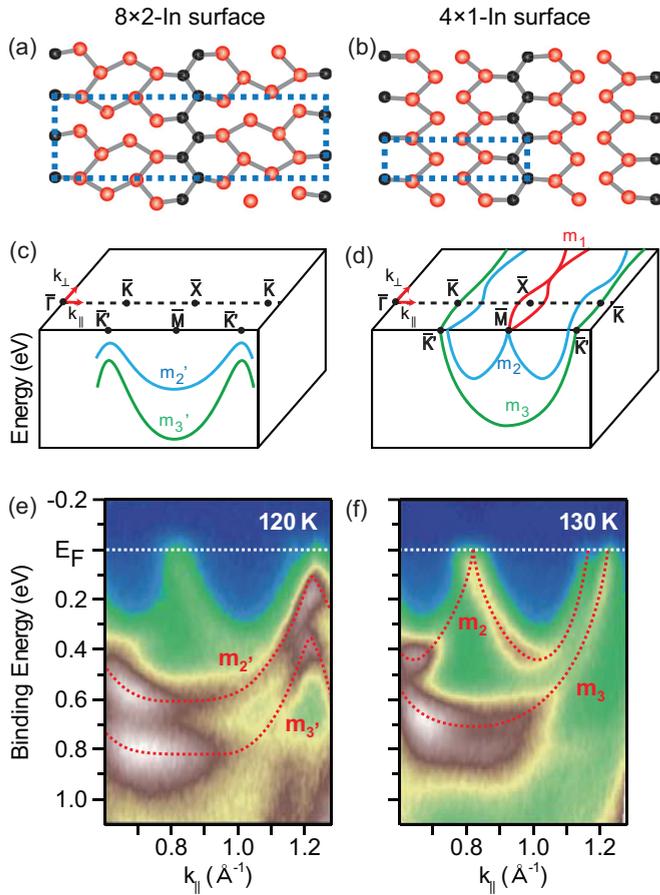


FIG. 1. (Color) Atomic and electronic band structures of the Si(111) 4×1 -In and 8×2 -In surfaces. Schematic atomic structure models of (a) the Si(111) 8×2 -In (Refs. 10,11 and 20) and (b) the Si(111) 4×1 -In (Ref. 21) surfaces. Red and black balls indicate In and Si atoms of the topmost layer, respectively. Schematics of Fermi contours and band dispersions (along \bar{K} - \bar{M} - \bar{K}) for the major surface states of (c) the 8×2 -In and (d) the 4×1 -In surfaces. The corresponding band dispersions measured at (e) 120 K and (f) 130 K. The surface state band dispersions are guided by dashed lines.

below 7.0×10^{-11} Torr. The Si(111) 4×1 -In surface was fabricated by depositing 1.5 ML of In on the Si(111) 7×7 surface at RT, followed by an annealing at 600 K, which drives the surface to reconstruct and evaporates surplus In adsorbates. O_2 molecules were dosed onto the Si(111) 4×1 -In surface at between 100 K and RT up to 10 langmuir (L) ($1.0 L = 10^{-6}$ torr-sec).

The Si(111) 4×1 -In surface is composed of two zigzag chains of In atoms close packed between Si chains [Fig. 1(b)].²¹ This In chain structure produces triple quasi-1D metallic surface states (so called m_1 , m_2 , and m_3) with different electron fillings (0.11, 0.38, and 0.50, respectively) and different degrees of interchain coupling, as shown in Figs. 1(d) and 1(f).^{1,22,23} The double In chain structure undergoes a phase transition into the 8×2 -In structure, which is composed of a hexagonlike arrangement of In atoms at 120–130 K [Fig. 1(a)].^{1,3,10} The hexagonlike structure is formed through the shear distortion between two In zigzag chains and the Peierls distortion along outer In atomic rows bonded with Si chains.^{10,11} The metallic band structure of the 4×1 -In

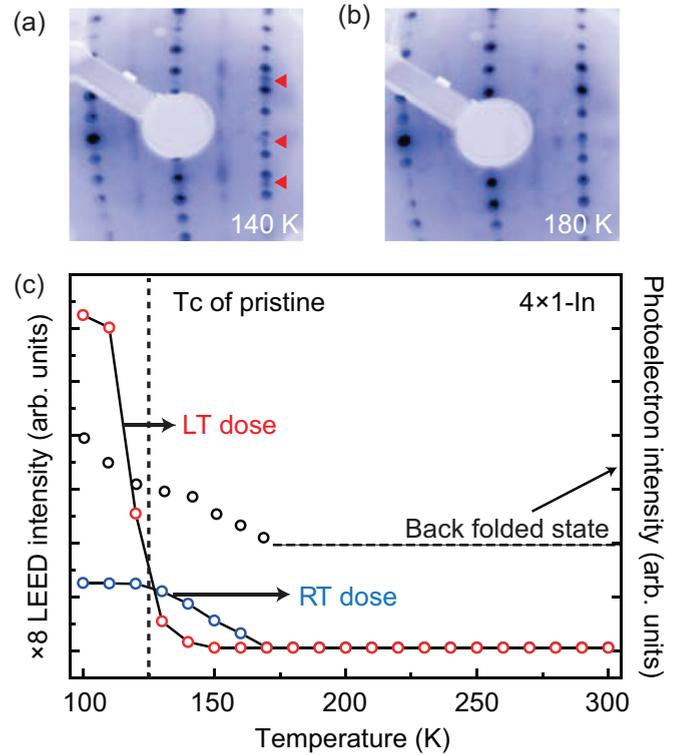


FIG. 2. (Color online) LEED patterns for the Si(111) 4×1 -In surface after the oxygen dose of 6 L at (a) 140 K and (b) 180 K. Note that the surface shows an apparent 8×2 LEED pattern at 140 K. (c) Intensities of the $\times 8$ diffraction spot and photoelectron intensities of the back folded surface band (m_3') as a function of the sample temperature for the surface with the 6 L oxygen exposure at RT. The LEED intensity data were also presented for the same oxygen dose but at about 140 K, which is essentially the same as those of the pristine Si(111) 4×1 -In surface.

surface changes into an insulating one as shown in Figs. 1(c) and 1(e).^{9,24} At first, the m_1 band energy shifts above the Fermi level (E_F) with its electrons transferred to the m_2 band through the shear distortion between the two In chains of a unit cell.^{10,11} Then, the m_2 and m_3 bands form band gaps at the $\times 2$ Brillouin zone boundary by the Peierls distortion.¹⁰ These two gaps, about 50–80 meV below the E_F for m_2' and 340–350 meV for m_3' , were called as the double Peierls gap.^{9,24} In experiments, intrinsic defects and imperfections of the surface can trap the 4×1 -In metallic domains locally well below T_c ,²⁵ and, thus, the faint trace of the metallic bands is usually observed below T_c as also shown in Fig. 1(e).^{9,24} In spite of these metallic traces, the metal-insulator transition can be most clearly indicated by the back foldings of the m_2' and m_3' bands, which are well correlated with the long range order of the 8×2 Peierls distortion represented by the $(1/8)$ th order spots in LEED.

III. RESULTS AND DISCUSSIONS

The previous study reported LEED patterns with different oxygen exposures and determined T_c of the 4×1 – 8×2 transition.¹⁴ Our own LEED study was very much consistent with this result. For example, Fig. 2 shows the result for the

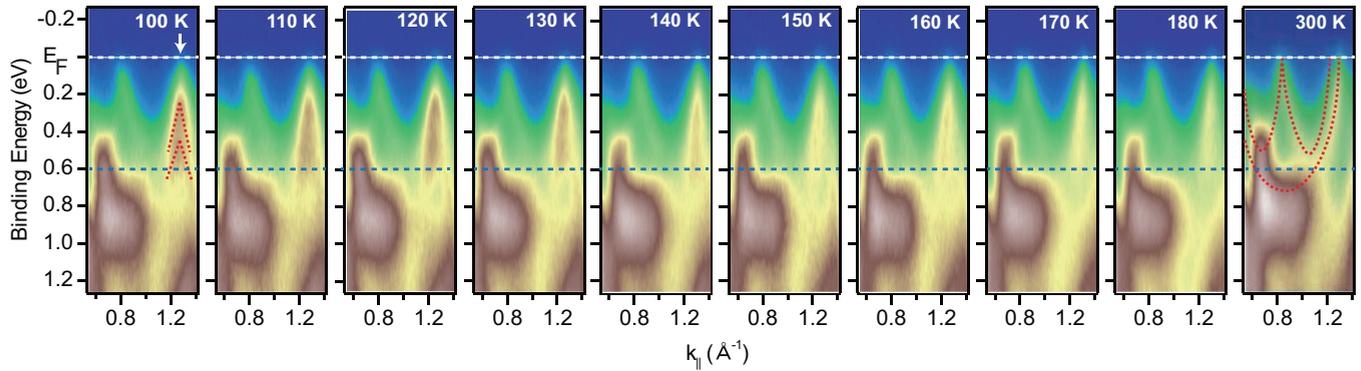


FIG. 3. (Color) Temperature-dependent ARPES measurements for quasi 1D surface states of the Si(111) 4×1 -In surface after the oxygen exposure of $6 L$ along the \bar{K} - \bar{M} - \bar{K}' . The back folded bands (m'_2 and m'_3 indicated by red dashed lines in the 100 K data) of the insulating phase disappear gradually at increasing temperature and are replaced by the metallic bands of the the pristine 4×1 -In surface. The metallic bands have their traces even at 100 K (see text).

$6 L$ oxygen dose on the 4×1 -In surface at RT. The LEED pattern at 140 K in Fig. 2(a) shows clearly the 8×2 pattern, which is distinct from that of the 4×1 phase at 180 K [Fig. 2(b)] indicating the increase of the apparent T_c . For the determination of the T_c , the intensity of the $\times 8$ diffraction spots was measured as a function of temperature as plotted in Fig. 2(c). The $\times 8$ spots develop from 170 K and saturates at 120 K. The T_c is increased by about 45 K. It is interesting to note that the T_c does not change for the same amount of oxygen dose at 140 K [the LEED intensity data also in Fig. 2(d)]. We think that an oxygen molecule does not dissociatively adsorb on the surface at this temperature. On the other hand, as shown in Fig. 2(c), the saturated intensity of the $\times 8$ spots is only about a quarter of that on the pristine 8×2 -In surface. This indicates that the oxygen-induced 8×2 surface is substantially disordered with only a quarter of the surface area are covered with well ordered and sufficiently large 8×2 domains.

In order to confirm that the oxygen adsorbates really increase the T_c of the 4×1 - 8×2 metal-insulator transition, we have to prove that the oxygen-induced 8×2 phase has the same band structure with that of the pristine 8×2 -In surface. Figure 3 shows the temperature-dependent ARPES data of the surface (along the \bar{K} - \bar{M} - \bar{K}' line of the surface Brillouin zone, see Fig. 1) from 100 to 300 K with a $6 L$ oxygen exposure. As mentioned above, the back folded bands of m'_2 and m'_3 are observed (red dashed lines) together with weaker traces of the metallic bands. The band back folding can be viewed more clearly in the momentum distribution curve (MDC) of the ARPES spectra at a binding energy of 0.6 eV (along the horizontal dashed line), which is shown in Fig. 4(a). The back folded band in Fig. 3 is indicated by the hatched components after the curve fitting with Lorentzian peaks. The distinction of this MDC from that of the metallic 4×1 -In surface [180 K data in Fig. 4(a)] is qualitative and unambiguous. As the temperature increases, the back folded bands gradually disappear leaving only the sharp metallic bands. We measured the spectral intensity of the back folded bands through the MDC fittings as shown in Fig. 4(a), which is then plotted in Fig. 2(c). The temperature dependence of the intensity of the back folded band is largely consistent with that of the 8×2 LEED pattern. This indicates clearly that the

oxygen-induced structural change is indeed due to the 4×1 - 8×2 metal-insulator transition and the metal-insulator T_c is indeed elevated by the oxygen impurity. The only noticeable difference between the temperature dependence of the ARPES and LEED data is the fact that the back folded band intensity in ARPES does not saturate even below 120 K. We suggest that this might be due to the larger laterally coherent domain size to produce a LEED pattern, while a further microscopy study is requested to understand this difference fully. We got consistent results, for ARPES and LEED measurements for a few different oxygen doses from 0.5 to 10 L , that the metal-insulator T_c is systematically ramped up by the oxygen does.

We also monitored the formation of the band gap at the zone boundary as a function of temperature as shown in Fig. 4(b). This gap evolution as measured by the leading edge shift is qualitatively consistent with ARPES intensity data for the band back folding. The measured apparent gap size of the oxygen-induced 8×2 phase is about 150 and 450 meV for m'_2 and m'_3 at $6 L$. The gap size seems to be increased but this apparent increase is thought to be largely related to the disorder on the surface introduced by the adsorbates as discussed below.

In addition, the doping effect of oxygen adsorbates is checked by measuring the band filling of the metallic bands with the MDC curve at the E_F at RT. The results are shown in Fig. 5(a). These data show clearly that the band fillings of m_2 and m_3 increase systematically as a function of the oxygen dose, about 7% at 10 L . This is in contrast with the assumption that an oxygen adsorbate dopes holes into this system.¹⁴ This behavior is qualitatively similar to the case of Na adsorbates.¹⁵ As mentioned above, in either case of the hole or electron doping, the metal-insulator T_c is expected only to decrease, that is, the pristine 4×1 -In surface is optimally doped.¹⁸ In the previous theoretical calculation, an oxygen adsorbate was shown to deplete metallic electrons on the adsorption site but increase on the neighboring In sites with little charge transfer in total.²⁶ On the other hand, if we monitor the ARPES spectral intensity at the E_F crossings upon the oxygen exposure [Fig. 5(b)], we can find that the density of states at E_F decreases systematically at RT. While this reduction resembles the opening of a gap, we cannot find

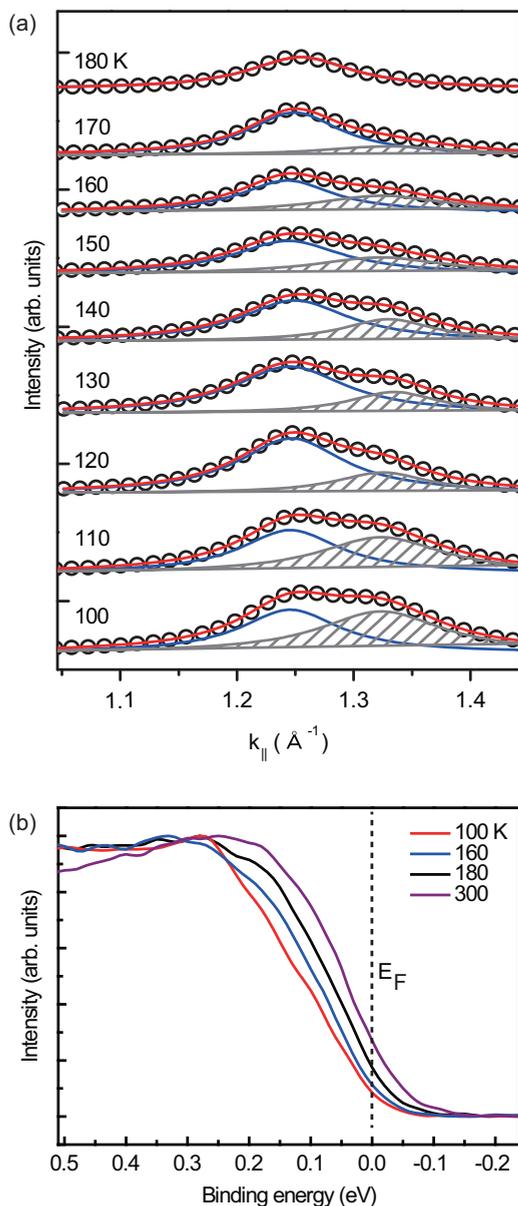


FIG. 4. (Color) (a) Momentum distribution curves of ARPES data along the horizontal dashed line in Fig. 3 (at a binding energy of 0.6 eV) as a function of temperature. These curves are fitted with two Lorentzian functions. The solid lines overlaid on the experimental data (circles) are the results of fits. The hatched peak of the decomposition indicates the back folded band. (b) Energy distribution curves of the ARPES data as a function of temperature at the $\times 2$ Brillouin zone boundary (indicated by an arrow in Fig. 3). Note that the leading edge of the spectra shift to a lower binding energy with increasing temperature.

any sign of the band back folding at this temperature. That is, this should be understood from the disordering induced by oxygen adsorbates, which is also indicated by the LEED study. The apparent gap size for the oxygen doses of 5–6 L is about 50 meV at RT, which explains the increase of the apparent gap size for the oxygen-induced 8×2 phase mentioned above. At low temperature after the oxygen adsorption, we also noticed an extra surface photovoltage shift, which tends to increase

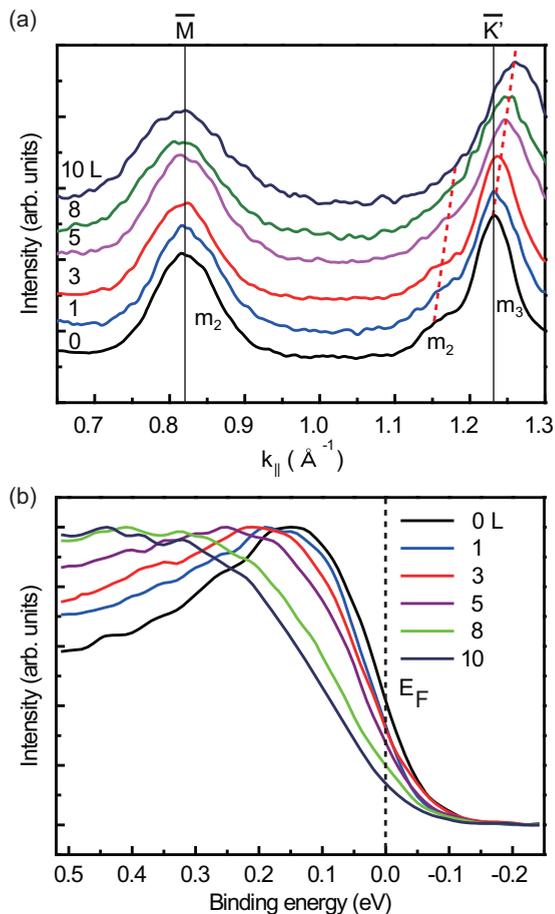


FIG. 5. (Color) (a) ARPES momentum distribution curves at the Fermi energy as a function of the oxygen exposure. (b) ARPES energy distribution curves at the Fermi level crossings of the m_3 band [along the dashed line in the right side of (a)]. This spectra are measured at 300 K.

the apparent gap size. These effects provide uncertainty to determine the gap size accurately at low temperature.

While the present result makes clear the elevated metal-insulator T_c by oxygen together with the substantial disorder, the mechanism is not clear at all. The previous study suggested that the elevated T_c can be due to the hole doping effect or to mobile oxygen adsorbates arranging themselves at low temperature. The present ARPES result clearly rules out the possibility of the hole doping. As mentioned above the hole doping is not expected to increase T_c in a theoretical point of view. We also think that mobile adsorbates are not likely since our RT STM study and theoretical calculation indicates that oxygen adsorbates are very much stable and not mobile. The possibility of the rearrangement of oxygen adsorbates upon cooling is thought to be not high but is to be examined by a variable temperature STM study.

It is evident that a further microscopic study is requested to understand the oxygen-induced increase of the metal-insulator T_c . In fact, even without any net charge transfer, an oxygen adsorbate would induce a local charge fluctuation and a local structural distortion. These electronic and structural perturbations would induce a Friedel oscillation of the charge density²⁷ and the local strain field decaying from the

adsorbate, respectively. In principle, there exist various ways in which these local structural and electronic perturbations can couple with the metal-insulator transition, where electronic, structural, and phononic degrees of freedom are all important. We thus stress that it would be very important to address the detailed bonding nature and the structure of oxygen adsorbates.

IV. CONCLUSIONS

We performed temperature-dependent ARPES and LEED study for the oxygen adsorption on the Si(111) 4×1 -In surface, which undergoes a well-known metal-insulator phase transition at 125 K. In accord with the recent reports, the oxygen adsorbates are shown to increase the transition temperature into the 8×2 phase systematically. However, the fraction of the 8×2 phase on the surface is reduced significantly after the oxygen does, which suggests a substantial disorder accompanied by the oxygen adsorption. The ARPES study clearly shows that the oxygen-induced 8×2 phase exhibits a consistent band structure with the insulating 8×2 phase of the pristine surface at low temperature. The temperature

evolution of the insulating bands is consistent with that of the LEED pattern of the oxygen-induced 8×2 phase. This proves unambiguously that the oxygen adsorption elevates the metal-insulator transition temperature. In addition, it was revealed that the oxygen adsorption increases the electron filling of metallic bands of the room temperature phase. The oxygen-induced disorder is consistently shown in ARPES spectra as the decreased spectral intensity of the metallic bands at room temperature. These results indicate that the elevated transition temperature cannot be simply understood from the doping effect by adsorbates. A further microscopic study is requested to understand the role of the oxygen impurity for the metal-insulator transition of this surface, where a novel interaction between an impurity and electronic, structural, and phononic degrees of freedom of a quasi-1D system might be revealed.

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